

Damage Mechanisms Affecting Fixed Equipment in the Refining Industry

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Contents

Page

1	Scope	1
2	Terms and Definitions	2
2.1	Definitions	2
2.2	Acronyms and Abbreviations	4
3	Damage Mechanisms	9
3.1	885 °F (475 °C) Embrittlement	9
3.2	Amine Corrosion	12
3.3	Amine Stress Corrosion Cracking	18
3.4	Ammonia Stress Corrosion Cracking	24
3.5	Ammonium Bisulfide Corrosion (Alkaline Sour Water)	28
3.6	Ammonium Chloride and Amine Hydrochloride Corrosion	33
3.7	Aqueous Organic Acid Corrosion	36
3.8	Atmospheric Corrosion	39
3.9	Boiler Water and Steam Condensate Corrosion	42
3.10	Brine Corrosion	45
3.11	Brittle Fracture	49
3.12	Carbonate Stress Corrosion Cracking	55
3.13	Carburization	65
3.14	Caustic Corrosion	69
3.15	Caustic Stress Corrosion Cracking	72
3.16	Cavitation	81
3.17	Chloride Stress Corrosion Cracking	86
3.18	CO₂ Corrosion	93
3.19	Concentration Cell Corrosion	98
3.20	Cooling Water Corrosion	101
3.21	Corrosion Fatigue	105
3.22	Corrosion Under Insulation	111
3.23	Creep and Stress Rupture	120
3.24	Dealloying [See Graphitic Corrosion (3.33) for Dealloying of Cast Iron]	126
3.25	Decarburization	130
3.26	Dissimilar Metal Weld Cracking	133
3.27	Erosion/Erosion-Corrosion	144
3.28	Ethanol Stress Corrosion Cracking	149
3.29	Flue Gas Dew Point Corrosion	157
3.30	Fuel Ash Corrosion	159
3.31	Galvanic Corrosion	164
3.32	Gaseous Oxygen-enhanced Ignition and Combustion	168
3.33	Graphitic Corrosion of Cast Irons	175
3.34	Graphitization	181
3.35	High-temperature H₂/H₂S Corrosion	186
3.36	High-temperature Hydrogen Attack	189
3.37	Hydrochloric Acid Corrosion	197
3.38	Hydrofluoric Acid Corrosion	200
3.39	Hydrofluoric Acid Stress Corrosion Cracking of Nickel Alloys	210
3.40	Hydrogen Embrittlement	213
3.41	Hydrogen Stress Cracking in Hydrofluoric Acid	219
3.42	Liquid Metal Embrittlement	221
3.43	Mechanical Fatigue (Including Vibration-induced Fatigue)	225

Contents

	Page
3.44 Metal Dusting	234
3.45 Microbiologically Influenced Corrosion	238
3.46 Naphthenic Acid Corrosion	244
3.47 Nitriding	248
3.48 Oxidation	252
3.49 Oxygenated Process Water Corrosion	258
3.50 Phenol (Carbolic Acid) Corrosion	261
3.51 Phosphoric Acid Corrosion	263
3.52 Polythionic Acid Stress Corrosion Cracking	265
3.53 Refractory Degradation	272
3.54 Stress Relaxation Cracking (Reheat Cracking)	274
3.55 Short-term Overheating-Stress Rupture (Including Steam Blanketing)	281
3.56 Sigma Phase Embrittlement.	286
3.57 Soil Corrosion	293
3.58 Sour Water Corrosion (Acidic).	297
3.59 Spheroidization (Softening)	300
3.60 Strain Aging	303
3.61 Sulfidation	305
3.62 Sulfuric Acid Corrosion	312
3.63 Temper Embrittlement.	316
3.64 Thermal Fatigue.	320
3.65 Thermal Shock.	327
3.66 Titanium Hydriding	329
3.67 Wet H ₂ S Damage (Blistering/HIC/SOHIC/SSC).	334
4 Process Unit Process Flow Diagrams	345
Annex A (informative) Useful Standards and References Relevant to this Recommended Practice	363
Annex B (informative) Technical Inquiries	367

Introduction

While ASME and API design codes and standards provide rules for the design, fabrication, inspection, and testing of new pressure vessels, piping systems, and storage tanks, they do not address equipment deterioration while in service, nor do they account for original fabrication defects not discovered during construction but found during subsequent inspections.

The interactions between the materials of construction and the environmental conditions to which they are exposed, including process conditions and external conditions, are extremely varied within an operating oil refinery. Oil refineries contain many different processing units, each having its own combination of process streams and temperature/pressure conditions. The purpose of this recommended practice is to describe the wide variety of service-induced damage and deterioration mechanisms, including corrosion and other types of metallurgical damage, that are most likely to affect the condition of the materials of construction commonly used in refinery equipment.

This document incorporates information gathered from major incidents in the refining industry and is intended to be consistent with applicable API documents as well as other related industry standards and practices. It is meant to provide guidance to pressure equipment integrity personnel but should not be considered the final technical basis for damage mechanism assessment and analysis or inspection and monitoring. The damage mechanism descriptions herein are not intended to provide a definitive guideline for every possible situation that may be encountered, and the reader may need to consult with an engineer or other corrosion specialist familiar with applicable degradation modes and failure mechanisms, particularly those that apply in special cases.

Damage Mechanisms Affecting Fixed Equipment in the Refining Industry

1 Scope

This recommended practice discusses damage mechanisms applicable to oil refineries; however, much of the information herein can also be applied to petrochemical and other industrial applications, as the user deems appropriate. It is up to the user to determine the applicability and appropriateness of the information contained herein as it applies to their facility.

API 571 is a reference document that provides useful information by itself and also complements other API standards and recommended practices. The document should be utilized as a reference to other integrity related documents. It is intended to contribute to the overall management of pressure equipment integrity and is a useful resource for many mechanical integrity program activities including:

- a) identification of existing damage or deterioration and anticipated rates of degradation,
- b) identification of future damage mechanism susceptibilities,
- c) development and maintenance of inspection and monitoring strategies, programs, and plans (e.g. per API 510, API 570, and API 653),
- d) implementation and monitoring of integrity operating windows (IOWs) (see API 584),
- e) development of corrosion control documents (CCDs) (see API 970),
- f) implementation of Risk-Based Inspection (RBI) programs (see API 580 and API 581),
- g) conducting Fitness-For-Service (FFS) assessments (see API 579-1/ASME FFS-1),
- h) application of proper examination techniques, and
- i) conducting pressure equipment integrity incident investigations (see API 585).

The information for each damage mechanism is provided in a set format as shown below.

- **Name of the Mechanism**—The term commonly used to describe or name the mechanism.
- **Description of Damage**—A basic description of the damage mechanism.
- **Affected Materials**—A list of the materials prone to the damage mechanism.
- **Critical Factors**—A list of factors that affect the damage mechanism (i.e. rate of damage).
- **Affected Units or Equipment**—A list of the affected equipment and/or units where the damage mechanism commonly occurs. This information is also shown on generic process flow diagrams (PFDs) for typical process units.
- **Appearance or Morphology of Damage**—A description of the damage mechanism, with pictures in some cases, to assist with recognition of the damage.
- **Prevention/Mitigation**—Methods to prevent or mitigate the damage and in some cases to evaluate by engineering analysis.

- **Inspection and Monitoring**—Guidance for nondestructive examination (NDE) and other methods for detecting, monitoring, characterizing, sizing, and determining the severity or extent of damage or deterioration.
- **Related Mechanisms**—A list of related damage mechanisms.
- **References**—A list of references cited, relied upon, or that provide background and other pertinent information.

Generic PFDs are provided in [Section 4](#) to assist the user in determining primary locations where some of the significant damage mechanisms are commonly found.

2 Terms and Definitions

2.1 Definitions

For the purposes of this document, the following definitions apply.

2.1.1

austenitic

A term that refers to a type of metallurgical structure (austenite) normally found in 300 series stainless steel (SS) and nickel-based alloys. These materials have a face centered cubic crystallographic structure and are generally nonmagnetic.

2.1.2

austenitic stainless steels

The 300 series SS, which commonly include Types 304, 304L, 304H, 309, 310, 316, 316L, 316H, 317, 317L, 321, 321H, 347, and 347H. The “L” and “H” suffixes refer to controlled ranges of low and high carbon content, respectively. These alloys are characterized by an austenitic structure.

2.1.3

carbon steel

An alloy consisting primarily of iron (Fe) with a small amount of carbon (C). Carbon steels do not have alloying elements intentionally added. However, there may be small amounts of elements permitted by specifications such as ASTM A516 and ASTM A106, for example, that can affect corrosion-related properties, hardness after welding, and toughness. Elements that may be found in small quantities include Mn, Cr, Ni, Mo, Cu, S, Si, P, Al, V, and B.

2.1.4

diethanolamine

DEA

Chemical used in amine treating to remove H₂S and CO₂ from hydrocarbon streams.

2.1.5

diglycolamine

DGA

Chemical used in amine treating to remove H₂S and CO₂ from hydrocarbon streams.

2.1.6

duplex stainless steel

A family of stainless steels that contain a mixed austenitic-ferritic structure including Alloys 2205, 2304, and 2507. The welds of 300 series SS may also exhibit a duplex structure.

2.1.7**ferritic**

A term that refers to a type of metallurgical structure (ferrite) normally found in carbon and low-alloy steels and many 400 series SS. These materials have a body centered cubic crystallographic structure and are generally magnetic.

2.1.8**ferritic stainless steels**

A family of stainless steels including Types 405, 409, 410S, 430, 442, and 446.

2.1.9**heat-affected zone****HAZ**

The portion of the base metal adjacent to a weld that has not been melted, but in which the metallurgical microstructure and mechanical properties have been changed by the heat of welding, sometimes with undesirable effects.

2.1.10**high-strength low-alloy steel****HSLA steel**

A family of carbon steels in which higher strength levels are achieved by the addition of moderate amounts of alloying elements such as titanium, vanadium, or niobium in amounts of less than 0.1 %. They can be more sensitive to cracking during fabrication from hydrogen embrittlement (HE) (delayed cracking; also known as underbead cracking).

2.1.11**low-alloy steel**

A family of steels containing up to 9 % chromium and other alloying additions for high temperature strength and creep resistance. The low-alloy steels commonly encountered in refining include C-0.5Mo, Mn-0.5Mo, 1Cr-0.5Mo, 1.25Cr-0.5Mo, 2.25Cr-1.0Mo, 5Cr-0.5Mo, and 9Cr-1Mo. These are considered ferritic steels, although their microstructures might be an alteration of the ferrite phase found in carbon steel.

2.1.12**martensitic**

A term that refers to a type of hard metallurgical structure (martensite) normally found in some 400 series SS. Heat treatment or welding followed by rapid cooling can sometimes produce this or a similar hard metallurgical structure in carbon and low-alloy steels. Martensitic and similar hard microstructures typically need to be tempered by heat treatment to soften them in order to make the material suitable for use in refining applications.

2.1.13**martensitic stainless steel**

A family of stainless steels including Types 410, 416, 420, 440A, 440B, and 440C.

2.1.14**methyl diethanolamine****MDEA**

Chemical used in amine treating to remove H₂S and CO₂ from hydrocarbon streams.

2.1.15**monoethanolamine****MEA**

Chemical used in amine treating to remove H₂S and CO₂ from hydrocarbon streams.

2.1.16**nickel-based**

A family of alloys containing nickel as a major alloying element (>30 % Ni) including Alloys 200, 400, K-500, 800, 800H, 825, 600, 600H, 617, 625, 718, X-750, and C276.

2.1.17**stainless steel**

An alloy of iron (Fe) with at least 10.5 % chromium (Cr) plus other alloy additions, depending on the specific grade. There are four major categories of stainless steels that are characterized by their metallurgical structure at room temperature: austenitic, ferritic, martensitic, and duplex. These alloys have varying amounts of chromium and other alloying elements that give them resistance to certain types of degradation depending on the alloy.

2.2 Acronyms and Abbreviations

For the purposes of this document, the following acronyms and abbreviations apply.

ABSA	angle beam spectral analysis
ACFM	alternating current field measurement
ACSCC	alkaline carbonate stress corrosion cracking
AET	acoustic emission testing
AGO	atmospheric gas oil
Al	aluminum
ARH	acid relief header
ARN	acid relief neutralizer
ASCC	alkaline stress corrosion cracking
AUBT	automated ultrasonic backscatter testing
AUT	automated ultrasonic testing
B	boron
BFW	boiler feedwater
C	carbon
C3	chemical symbol referring to propane or propylene
C4	chemical symbol referring to butane or butylene
Cat	catalyst or catalytic
CCR	continuous catalytic reforming
CH ₄	methane
Cl ⁻ SCC	chloride stress corrosion cracking
CO	carbon monoxide
CO ₂	carbon dioxide

Cr	chromium
Cu	copper
CuF	cuprous fluoride
CuF ₂	cupric fluoride
CUI	corrosion under insulation
CVN	Charpy V-notch
CW	cooling water
DEA	diethanolamine
DGA	diglycolamine
DIPA	diisopropylamine
DMW	dissimilar metal weld
DNB	departure from nucleate boiling
ECT	eddy current testing
EMAT	electromagnetic acoustic transducer
FAC	flow accelerated corrosion (in boiler water and steam condensate)
FCC	fluid catalytic cracker
Fe	iron
Fe ₃ O ₄	magnetite
FeS	iron sulfide
FFS	Fitness-For-Service
FGE	fuel grade ethanol
FMR	field metallographic replication
FRP	fiber-reinforced plastic
GWT	guided wave testing
H ₂	diatomic hydrogen gas
HAZ	heat-affected zone
HB	Brinell hardness number
HCGO	heavy coker gas oil
HCl	hydrochloric (acid)
HCN	hydrogen cyanide
H ₂ CO ₃	carbonic acid

HE	hydrogen embrittlement
HF	hydrofluoric (acid)
Hg	mercury
HHPS	hot high-pressure separator
HIC	hydrogen-induced cracking
HP	high pressure
HPS	high-pressure separator
HRC	Rockwell hardness number (based on Rockwell C scale)
HRSG	heat-recovery steam generator
H ₂ S	hydrogen sulfide
HSAS	heat stable amine salts
HSLA	high-strength low-alloy
H ₂ SO ₄	sulfuric acid
HCO	heavy cycle oil
HTHA	high-temperature hydrogen attack
HVGO	heavy vacuum gas oil
ID	inside diameter
IOW	integrity operating window
IRIS	internal rotating inspection system
K.O. or KO	knock out, as in K.O. drum
KOH	potassium hydroxide
LCGO	light coker gas oil
LCO	light cycle oil
LP	low pressure
LPS	low-pressure separator
LVGO	light vacuum gas oil
MAWP	maximum allowable working pressure
MDEA	methyl diethanolamine
MDMT	minimum design metal temperature
MEA	monoethanolamine
MFL	magnetic flux leakage

MIC	microbiologically influenced corrosion
Mn	manganese
Mo	molybdenum
MPT	minimum pressurization temperature
mpy	mils per year
MT	magnetic particle testing
MVP	materials verification program
Na	sodium
NAC	naphthenic acid corrosion
NaOH	sodium hydroxide
Nb	niobium
NDE	nondestructive examination
NFT	near-field testing
NH ₃	ammonia
NH ₄ HS	ammonium bisulfide
Ni	nickel
NO ₂	nitrogen dioxide
NPSH	net positive suction head
O ₂	oxygen
OD	outside diameter
P	phosphorus
PAUT	phased array ultrasonic testing
PEC	pulsed eddy current
PFD	process flow diagram
PMI	positive materials identification
POX	partial oxidation
PREN	pitting resistance equivalent number
PT	liquid penetrant testing
PTA SCC	polythionic acid stress corrosion cracking
PTFE	polytetrafluoroethylene
PVC	polyvinyl chloride

PWHT	postweld heat treatment
RE	residual element
RFT	remote field testing
RT	radiographic testing
S	sulfur
SAW	submerged-arc welding
SCC	stress corrosion cracking
SEM	scanning electron microscope
Si	silicon
SLOFEC	saturated low-frequency eddy current
SO ₂	sulfur dioxide
SOHIC	stress-oriented hydrogen-induced cracking
SRB	sulfate-reducing bacteria
SRC	stress relaxation cracking
SRU	sulfur recovery unit
SS	stainless steel
SSC	sulfide stress cracking
SW	sour water
SWS	sour water stripper
SWUT	shear wave ultrasonic testing
TAN	total acid number
Ti	titanium
TOFD	time of flight diffraction
UT	ultrasonic testing
UTS	ultimate tensile strength
V	vanadium
VT	visual inspection (visual testing)
WFMT	wet fluorescent magnetic particle testing
Zn	zinc

3 Damage Mechanisms

This section describes the damage mechanisms found in refinery equipment. It includes low- and elevated-temperature corrosion, metallurgical and mechanical damage, environment-assisted cracking, and a few mechanisms that do not necessarily fit into any of these categories.

Section 4 contains PFDs for process units commonly found in refining. These PFDs show the location in the unit where specific damage mechanisms are most likely to be found.

3.1 885 °F (475 °C) Embrittlement

3.1.1 Description of Damage

885 °F (475 °C) embrittlement is a loss of ductility and fracture toughness due to a metallurgical change that can occur in stainless steels containing a ferrite phase as the result of exposure in the temperature range 600 °F to 1000 °F (315 °C to 540 °C). The embrittlement can lead to cracking failure.

3.1.2 Affected Materials

- a) 400 series SS (e.g. 405, 409, 410, 410S, 430, and 446).
- b) Duplex stainless steels such as Alloys 2205, 2304, and 2507.
- c) Austenitic (300 series) stainless steel weld metals, which normally contain up to about 10 % ferrite phase to prevent hot cracking during welding.

3.1.3 Critical Factors

- a) The alloy composition, particularly chromium content, amount of ferrite phase, and operating temperature are critical factors.
- b) The lower-chromium alloys (e.g. 405, 409, 410, and 410S) are less susceptible to embrittlement. The higher chromium ferritic stainless steels [e.g. 430 (16 % to 18 % Cr) and 446 (23 % to 27 % Cr)] and duplex stainless steels (22 % to 25 % Cr) are much more susceptible.
 - 1. Although it has not yet been shown in all 300 series SS weld metals, Charpy impact testing of Type 308 and Type 347H SS weld metal aged in approximately the 850 °F to 885 °F (455 °C to 475 °C) temperature range has found evidence of 885 °F (475 °C) embrittlement, with individual sample results in some cases being less than 15 ft-lb (20 J) at ambient temperatures. However, 885 °F (475 °C) embrittlement of austenitic stainless steel weld metal historically has not been found to be a significant concern in typical refining applications.
- c) Increasing amounts of ferrite phase in duplex stainless steels increase susceptibility to damage when operating in the high-temperature range of concern. A dramatic increase in the ductile-to-brittle transition temperature will occur. Duplex stainless steels also need to be cooled rapidly after welding to avoid formation of embrittling phases.
- d) High-temperature exposure is required for embrittlement. A primary consideration is operating time at temperature within the critical temperature range. Damage is cumulative and results from the formation of an embrittling ordered metallic phase (alpha prime phase) that occurs most readily at approximately 885 °F (475 °C). Additional time is required to reach maximum embrittlement at temperatures above or below 885 °F (475 °C). For example, many thousands of hours may be required to cause embrittlement at 600 °F (315 °C).
- e) As a practical matter, since equipment is typically in service for years, it is often assumed that susceptible materials that have been exposed to temperatures in the 600 °F to 1000 °F (370 °C to 540 °C) range are affected.
- f) The effect on toughness is not pronounced at the operating temperature but is significant at lower temperatures experienced during plant shutdowns, start-ups, or upsets.

- g) Embrittlement can also result from heat treatment if the material is held within or cooled slowly through the embrittlement range.

3.1.4 Affected Units or Equipment

- a) 885 °F (475 °C) embrittlement can be found in any unit where susceptible alloys are exposed to the embrittling temperature range.
- b) Most refining companies limit the use of ferritic stainless steels to non-pressure-boundary applications because of this damage mechanism.
- c) Common examples include fractionator trays and internals in high-temperature vessels used in crude, vacuum, fluid catalytic cracker (FCC), and coker units. Typical failures include cracking when attempting to weld or to straighten bent, upset tower trays made of Type 409 and 410 SS. (This occurs often with vacuum tower trays of this material.)
- d) Other examples include duplex stainless steel heat exchanger tubes and other components exposed to temperatures above 600 °F (315 °C) for extended time periods. Duplex stainless steels are normally limited to a maximum service temperature of 600 °F (315 °C).

3.1.5 Appearance or Morphology of Damage

- a) 885 °F (475 °C) embrittlement is a metallurgical change that is not readily apparent with metallography.
- b) The existence of 885 °F (475 °C) embrittlement can possibly be identified by an increase in hardness in affected areas. Failure during bend testing or impact testing of samples removed from service is the most positive indicator of 885 °F (475 °C) embrittlement. ([Figure 3-1-1](#))
- c) Most cases of embrittlement are found in the form of cracking during turnarounds or during start-up or shutdown when the material is at lower temperature where the effects of embrittlement are most detrimental. Embrittled 410 SS has been shown to require a temperature of about 350 °F (175 °C) before adequate toughness has been restored.

3.1.6 Prevention/Mitigation

- a) The best way to prevent 885 °F (475 °C) embrittlement is to avoid exposing the susceptible material to the embrittling range or to use a non-susceptible material. In some cases, users accept the possibility of embrittlement of non-pressure-containing components, e.g. trays and other internals, and deal with the possibility or consequences during maintenance.
- b) Cracking of embrittled material can often be avoided through temperature controls during start-up and shutdown.
- c) It is possible to minimize the effects of embrittlement through modifications in the chemical composition of the alloy; however, resistant material may not always be readily available in most commercial forms.
- d) 885 °F (475 °C) embrittlement is reversible by heat treatment followed by rapid cooling. The de-embrittling heat treatment temperature is typically 1100 °F (595 °C) or higher and may not be practical for many equipment items. If the de-embrittled component is exposed to the same service conditions, it will re-embrittle faster than it did initially.

3.1.7 Inspection and Monitoring

This damage mechanism is very difficult to find prior to equipment failure. It is also time dependent and may take a while to develop in service. Online inspection is not applicable. Awareness of susceptible equipment can help direct inspection planning.

- a) The most effective method of detecting or confirming 885 °F (475 °C) embrittlement is removing and impact or bend testing a sample of the suspect material. Failure during a simple bend test is the most common

method of confirming 885 °F (475 °C) embrittlement in thin components like tower trays. Metallographic examination is typically not effective because the embrittlement-causing phase in the microstructure is so difficult to find or see.

- b) Cracking may be visually apparent in certain types of trays and other non-pressure-containing hardware that have cracked during maintenance or repair activities.
- c) Field hardness testing may distinguish embrittled from non-embrittled material, but hardness testing alone is generally not definitive. Also, the hardness test itself may produce cracking, depending on the degree of embrittlement.
- d) Hammer testing ("field impact testing") is considered a destructive test. Tapping a suspect component with a hammer may crack the component, depending on the degree of embrittlement. Hammer testing might confirm that a component is not badly embrittled, if it does not crack, or that it is embrittled, if it does crack.

3.1.8 Related Mechanisms

Sigma phase embrittlement (3.56).

3.1.9 References

1. *High-temperature Characteristics of Stainless Steels, Designers' Handbook Series*, American Iron and Steel Institute, Washington, DC, 1979.
2. G.E. Moller, "Experiences with 885 °F (475 °C) Embrittlement in Ferritic Stainless Steels," *Materials Protection*, NACE International, May 1966.
3. S.A. David, J.M. Vitek, and D.J. Alexander, "Embrittlement of Austenitic Stainless Steel Welds," Office of Scientific and Technical Information Technical Reports, (University of North Texas Libraries Government Documents Department, <https://digital.library.unt.edu/ark:/67531/metadc741815/>), June 1995.

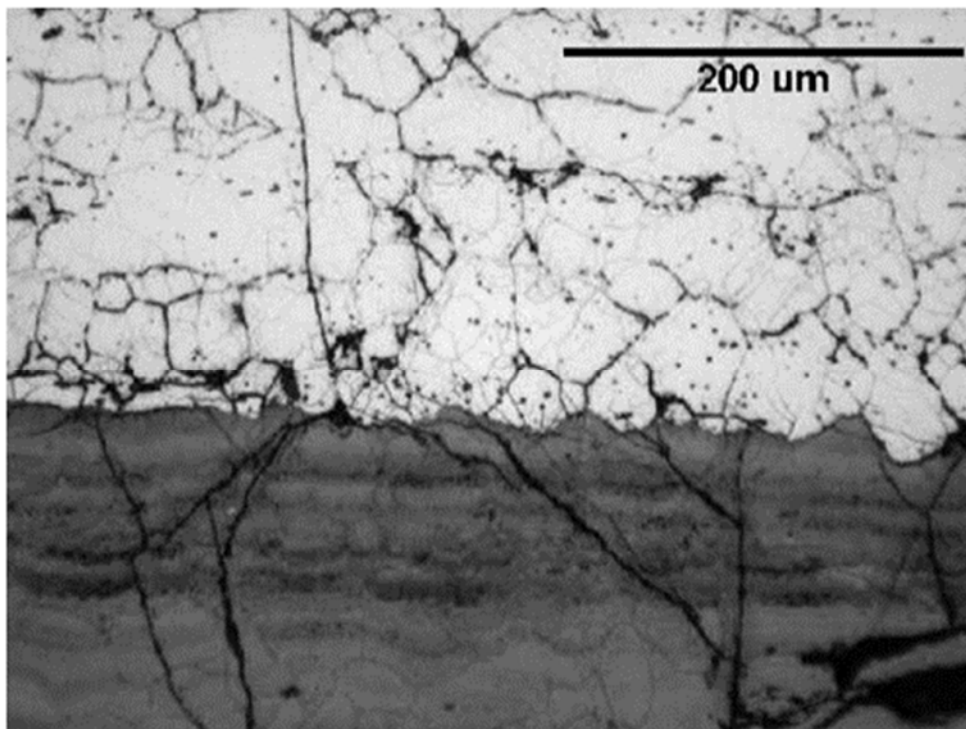


Figure 3-1-1—Sample of cracked material with intergranular cracks visible in the microstructure, suggesting severe embrittlement.

3.2 Amine Corrosion

3.2.1 Description of Damage

- a) Amine corrosion is typically localized corrosion that occurs principally on carbon steel in amine treating processes. Corrosion is not caused by the amine itself but results from dissolved acid gases (CO_2 and H_2S), heat stable amine salts (HSAS), amine degradation products (e.g. bicine, oxalate, and formate salts), and other contaminants.
- b) SCC of carbon steel in amine services is discussed in 3.3.

3.2.2 Affected Materials

Primarily carbon steel. 300 series SS and other grades of stainless steel are more resistant.

3.2.3 Critical Factors

- a) Corrosion depends on design and operating practices, the type of amine, contaminants, temperature, and velocity.
- b) Amine corrosion is very closely tied to the operation of the unit. With a few exceptions, carbon steel is suitable for most components in a properly designed and operated unit. Most problems can be traced to faulty design, poor operating practices, or solution contamination.
- c) Corrosion is also dependent on the type of amine used. In general, alkanolamine systems can be rated in order of aggressiveness from most to least as follows: monoethanolamine (MEA), diglycolamine (DGA), diisopropylamine (DIPA), diethanolamine (DEA), and methyl diethanolamine (MDEA).
- d) Lean amine solutions are generally not corrosive because they have low conductivity and high pH. However, an excessive accumulation of heat stable salts, e.g. bicine, oxalate, formate, and acetate salts above about 2 %, depending on the amine, can significantly increase corrosion rates in hot lean amine.
- e) Oxygen in-leakage causes high corrosion rates and contributes to heat stable salt formation.
- f) Lean amine solutions contain a small amount of H_2S , which helps maintain a stable iron sulfide film. Overstripped lean amine solutions can be corrosive if there is inadequate H_2S present to maintain the protective iron sulfide film.
- g) Corrosion rates increase with increasing temperature, particularly in rich amine service. Temperatures above about 220 °F (105 °C) can result in acid gas flashing, if the pressure drop is high enough, with severe localized corrosion.
- h) Process stream velocity will influence the amine corrosion rate and nature of attack. Corrosion is generally uniform; however, high velocities and turbulence will cause localized thickness losses. For carbon steel, velocities are generally limited to 3 fps to 6 fps (1 m/s to 2 m/s) for rich amine and about 20 fps (6 m/s) for lean amine.

3.2.4 Affected Units or Equipment

- a) Amine units, which remove H_2S , CO_2 , and mercaptans from process streams in many units including crude, coker, FCC, hydrogen-reforming, hydroprocessing, and tail gas units.
- b) The regenerator reboiler, including the feed and return lines, and the regenerator are areas where the temperature and turbulence are the highest in the amine system and therefore are locations of potentially significant corrosion.
 - 1. If excessive regeneration occurs in the reboiler (i.e. > 5 % of the total amine regeneration occurs in the reboiler), it can lead to acid gas corrosion in the reboiler, its vapor return line, and the bottom of the regenerator.

2. Ammonia, H₂S, and hydrogen cyanide (HCN) accelerate corrosion in the regenerator overhead condenser and outlet piping as well as reflux piping, valves, and pumps.
- c) The rich amine side of the lean/rich exchangers, the hot lean amine piping, the hot rich amine piping, the stripper overhead condenser piping, the amine solution pumps, and the reclaimers are also areas where corrosion problems commonly occur.
- d) In amine absorber systems, the locations most susceptible to amine corrosion are where amine or acid gas impinge on the shell, as well as downstream of pressure letdown valves and other areas of high velocity in the rich amine piping.

3.2.5 Appearance or Morphology of Damage

- a) Carbon steel and low-alloy steels mostly suffer uniform thinning in localized (isolated) locations or localized under-deposit attack. (Figure 3-2-1 to Figure 3-2-6)
- b) When the process stream velocity is low, thinning will be more uniform and widespread. At locations with high velocity or turbulence, it will be more localized with greater metal loss.
- c) Welds can be preferentially attacked. (Figure 3-2-1 and Figure 3-2-3)

3.2.6 Prevention/Mitigation

- a) Proper operation to the amine system is the most effective way to control corrosion, with particular attention paid to acid gas loading levels. In addition, to avoid corrosive amine degradation products, the process temperature should not exceed recommended limits. Proper control of the reboiler rate and temperature is necessary in order to maintain proper regenerator temperatures.
- b) Proper attention should be given to avoiding the buildup of heat stable salts to unacceptable levels.
- c) The system design should incorporate measures to control local pressure drop to minimize flashing. In areas where it is unavoidable, upgrading to 300 series SS or other corrosion-resistant alloys may be needed. Type 410 SS trays and internals are commonly used in absorber and stripping towers.
- d) Avoid air ingress into the system as this will lead to formation of corrosive heat stable salts.
- e) Storage tanks and surge vessels should be blanketed with oxygen-free inert gas to prevent introduction of oxygen and in-leakage of air.
- f) Solids and hydrocarbons should be removed from the amine solution by filtration and through process control.
- g) Corrosion inhibitors may be required to control amine corrosion within acceptable levels.

3.2.7 Inspection and Monitoring

- a) Visual inspection (VT) of internal surfaces at flow impingement areas, turbulent flow areas, liquid/vapor interfaces, and of welds/heat-affected zones (HAZs) is effective in identifying localized corrosion. Sometimes a pit gauge is used in conjunction with visual examination to provide specific data on extent of metal loss.
- b) Thin regions:
 1. external ultrasonic testing (UT) is typically used to map the thickness of components to identify local thin regions;
 2. profile radiographic testing (RT) can be effective for identifying localized attack, particularly at welds/HAZs and turbulent locations;

3. UT can sometimes be used in conjunction with VT, laser scanning, structured white light imaging, and/or pit gauges to determine the extent of metal loss.
- c) Permanently mounted thickness monitoring sensors can be used.
- d) Corrosion monitoring can be performed by installing corrosion coupons and/or inserting corrosion probes.
- e) The level of amine degradation products (e.g. bicine, oxalate, and formate salts), should be monitored. An increase in iron content of the amine solution will coincide with an increase in the level of these degradation products.
- f) Fouling of exchangers and filters can be a sign of corrosion problems on the unit.

3.2.8 Related Mechanisms

Amine SCC (3.3).

3.2.9 References

1. J. Gutzeit, "Refinery Corrosion Overview," *Process Industries Corrosion—The Theory and Practice*, NACE International, Houston, TX, 1986, pp. 171–189.
2. L.R. White and D.E. Street, "Corrosion Control in Amine Treating Units," *Proceedings of the Special Symposium on Corrosion in the Oil Refining Industry*, NACE International, Houston, TX, 1996.
3. R.B. Nielsen et al., "Corrosion in Refinery Amine Systems," Paper No. 571, *Corrosion/95*, NACE International, Houston, TX.
4. API Recommended Practice 945, *Avoiding Environmental Cracking in Amine Units*, American Petroleum Institute, Washington, DC.
5. M.A. Saleem and A.A. Hulaibi, "Corrosion Challenges in Gas Treating Units," Paper No. 08416, *Corrosion/2008*, NACE International, Houston, TX.
6. P. Quiroga et al., "Improving Amine Unit Reliability with On-line Corrosion Monitoring & Modeling," Paper No. 08421, *Corrosion/2008*, NACE International, Houston, TX.
7. D. Fan et al., "Role of Impurities and H₂S in Refinery Lean DEA System Corrosion," Paper No. 00495, *Corrosion/2004*, NACE International, Houston, TX.



Figure 3-2-1—Localized amine corrosion at the weld found in piping from the reboiler to the regenerator tower in an MEA unit. Many other similar cases were found, some going as deep as half thickness. They were originally found with shear wave UT inspection and mistaken as cracks.



Figure 3-2-2—Hot lean amine corrosion of carbon steel attributed to increased CO₂ content in the MEA solution.



Figure 3-2-3—Preferential weld corrosion in lean amine. (Reference 5)



Figure 3-2-4—Preferential corrosion in an amine regenerator reboiler return elbow. (Reference 6)

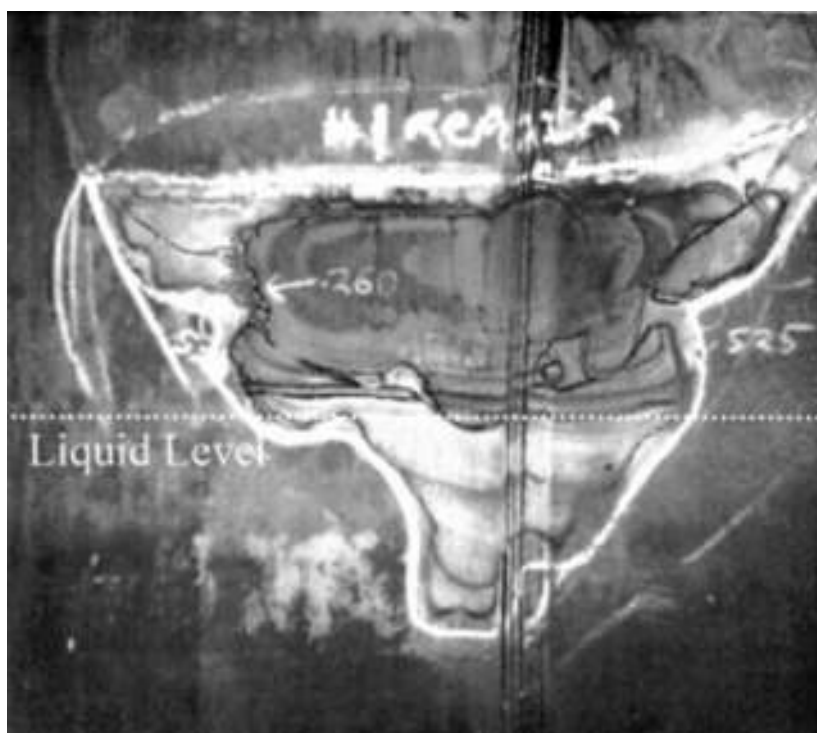


Figure 3-2-5—Corrosion near the liquid level in a reboiler exchanger shell from an amine regeneration unit. (Numbers drawn on figure are UT thicknesses in inches.)
Nominal wall: 0.550 in. (Reference 7)

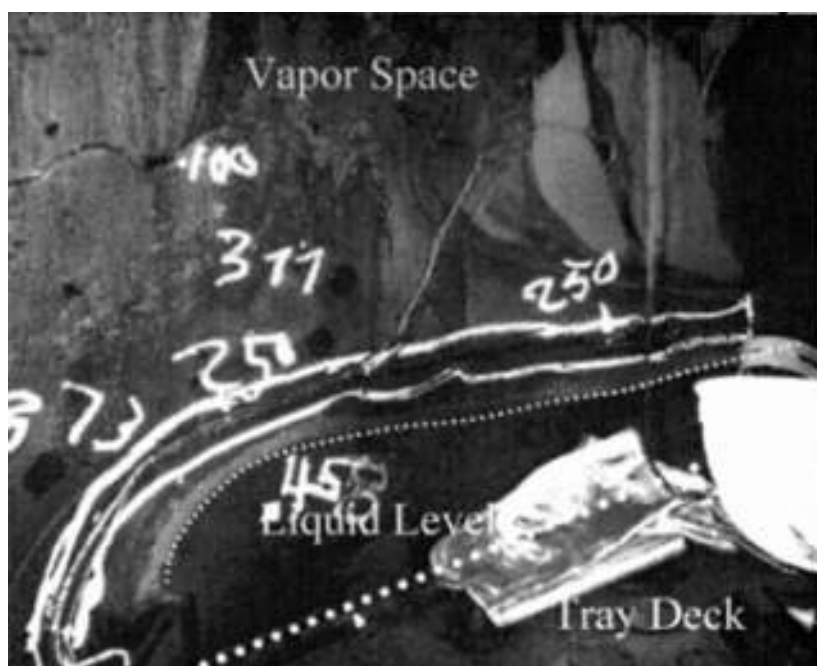


Figure 3-2-6—Corroded amine regenerator column shell near a downcomer. (Numbers drawn on figure are UT thicknesses in inches.) Nominal wall: 0.5 in. (Reference 7)

3.3 Amine Stress Corrosion Cracking

3.3.1 Description of Damage

- a) Amine SCC (or amine cracking) is the cracking of steels under the combined action of tensile stress and an aqueous alkanolamine solution used to remove (absorb) H_2S and/or CO_2 and their mixtures from various gas and liquid hydrocarbon streams.
- b) Amine cracking is a form of alkaline stress corrosion cracking (ASCC).
- c) It is most often found at or adjacent to non-postweld-heat-treated (non-PWHT'd) carbon steel welds or in highly cold worked parts.
- d) Amine cracking should not be confused with several other types of SCC that can occur in amine environments, which are further described in [3.66](#) and [3.12](#).

3.3.2 Affected Materials

Carbon steel and low-alloy steels.

3.3.3 Critical Factors

- a) The critical factors are the level of tensile stress, the type of amine, and temperature.
- b) Increasing stress level increases the likelihood and severity of cracking. Cracking is most often associated with high residual stresses from welding or cold working that have not been removed by an effective stress-relieving heat treatment.
- c) Cracking is more likely to occur in MEA and DEA services, but is also found in most amines including MDEA and DIPA (ADIP).
- d) Increasing temperature increases the likelihood and severity of cracking; however, cracking has been reported down to ambient temperatures with some amines, MEA in particular. Other than in special cases (such as where the steel component is completely clad or overlaid with stainless steel or other alloy and the welds are not exposed), PWHT is now commonly recommended for all lean amine systems (excluding fresh amine) at all operating temperatures, regardless of amine type. Some refiners also PWHT'd rich amine service equipment, whether for amine SCC resistance, wet H_2S [SSC and stress-oriented hydrogen-induced cracking (SOHIC)] resistance, or both. Refer to API 945 for guidelines on PWHT for various amine services.
- e) Amine cracking is most often associated with lean amine services, where a solution of amine and water is used. The pure alkanolamine does not cause cracking. In rich amine services in H_2S removal systems, the H_2S helps form an iron sulfide (FeS) film on steel surfaces that helps impede amine SCC. Cracking in rich amine services is most often associated with wet H_2S . (See [3.67](#).)
- f) Cracking can occur in non-PWHT'd piping and equipment as the result of exposure to steam out and to short-term amine carryover. This is another reason PWHT (for stress relief) is now commonly recommended regardless of operating temperature.
- g) Amine concentration does not appear to have a significant effect on the propensity for cracking.

3.3.4 Affected Units or Equipment

All non-PWHT'd carbon steel piping and equipment in amine service, including contactors, absorbers, strippers, filters, regenerators, and heat exchangers, as well as any equipment subject to amine carryover, are subject to cracking. Equipment in rich amine service is less susceptible than equipment in lean amine service, but not necessarily immune, especially vessels where acid gas is either entering the amine (making rich amine) or leaving the amine (making lean amine).

3.3.5 Appearance or Morphology of Damage

- a) Amine SCC cracks initiate on the (process side) surface of piping and equipment, primarily at welds. Cracks can appear in the HAZ and/or the weld metal but are most often found in the high residual stress zone, which is typically beyond the metallurgical HAZ, about a tenth of an inch or more (several millimeters) from the weld. (Figure 3-3-1)
- b) Cracking typically develops parallel to the weld, and there may be multiple parallel cracks. In weld metal, the cracks are either longitudinal or transverse to the weld.
- c) At set-on nozzles, the cracks are radial in the base metal, i.e. they fan out from the bore. (Figure 3-3-2)
- d) At set-in nozzles, the cracks are usually parallel to the weld.
- e) The appearance of the cracks on the surface may be similar to those caused by wet H₂S cracking.
- f) Because residual stress is a driving force for cracking, cracks can occur on the process side opposite external attachment welds.
- g) Positive identification of amine cracking can be confirmed by metallographic analysis. The cracking is typically intergranular and oxide filled with some branching. (Figure 3-3-1 and Figures 3-3-3 to 3-3-5)

3.3.6 Prevention/Mitigation

- a) Carbon steel welds in piping and equipment should be stress relieved in accordance with API 945 and NACE SP0472. The recommended minimum stress-relief temperature is 1175 ± 25 °F (635 ± 15 °C). The same recommendation applies to repair welds and to internal and external attachment welds. (See Figure 3-3-6.) For local PWHT, recommended heat treatment band width is listed in NACE SP0472 with reference to WRC 452.
- b) Consider using solid or clad stainless steel or other corrosion-resistant alloys in lieu of carbon steel.
- c) Thoroughly water wash non-PWHT'd carbon steel piping and equipment prior to welding, heat treatment, or steam out.

3.3.7 Inspection and Monitoring

- a) Wet fluorescent magnetic particle testing (WFMT), alternating current field measurement (ACFM), and eddy current testing (ECT) can be effective techniques to detect these surface-breaking cracks. Proper surface preparation by grit blasting, high-pressure water blasting, flapper wheel abrasive grinding, or other method is required to remove scale and contaminants. The method of surface preparation is dependent upon the specific technique.
- b) Angle beam [shear wave ultrasonic testing (SWUT) and phased array ultrasonic testing (PAUT)] ultrasonic techniques can be effective to detect and size cracks and would be the methods typically used for piping; however, caution must be exercised when interpreting results on piping welds that have not previously been inspected with angle beam UT (SWUT or PAUT) as it may be difficult to distinguish SCC from original fabrication flaws. SWUT and PAUT can also be used to periodically monitor crack growth.
- c) Liquid penetrant testing (PT) may be used but should not be the only means of detection. PT may not be effective in finding tight cracks because the cracks are oxide filled.
- d) RT may not be effective in detecting fine, tight cracks.
- e) Acoustic emission testing (AET) can be used for locating cracks and monitoring crack growth.

3.3.8 Related Mechanisms

Caustic SCC (3.15) and carbonate SCC (3.12) are other forms of ASCC that are similar in appearance. Ammonia SCC of carbon steel (3.4) is also similar in appearance.

3.3.9 References

1. API Recommended Practice 945, *Avoiding Environmental Cracking in Amine Units*, American Petroleum Institute, Washington, DC.
2. "Fitness-For-Service Evaluation Procedures for Operating Pressure Vessels, Tanks, and Piping in Refinery and Chemical Service," Materials Properties Council, FS-26, Draft No. 5, Consultants Report, NY, 1995.
3. J. Gutzeit and J.M. Johnson, "Stress Corrosion Cracking of Carbon Steel Welds in Amine Service," *Materials Performance*, Vol. 25, No. 7, 1986, p.18.
4. J.P. Richert et al., "Stress Corrosion Cracking of Carbon Steel in Amine Systems," Paper No. 187, *Corrosion/87*, NACE International, Houston, TX.
5. A. Bagdasarian et al., "Stress Corrosion Cracking of Carbon Steel in DEA and ADIP Solutions," *Materials Performance*, 1991, pp. 63–67.
6. NACE SP0472, *Methods and Controls to Prevent In-service Environmental Cracking of Carbon Steel Weldments in Corrosive Petroleum Refining Environments*, NACE International, Houston, TX.
7. WRC Bulletin 452, *Recommended Practices for Local Heating of Welds in Pressure Vessels*, Welding Research Council, Shaker Heights, OH, June 2000.

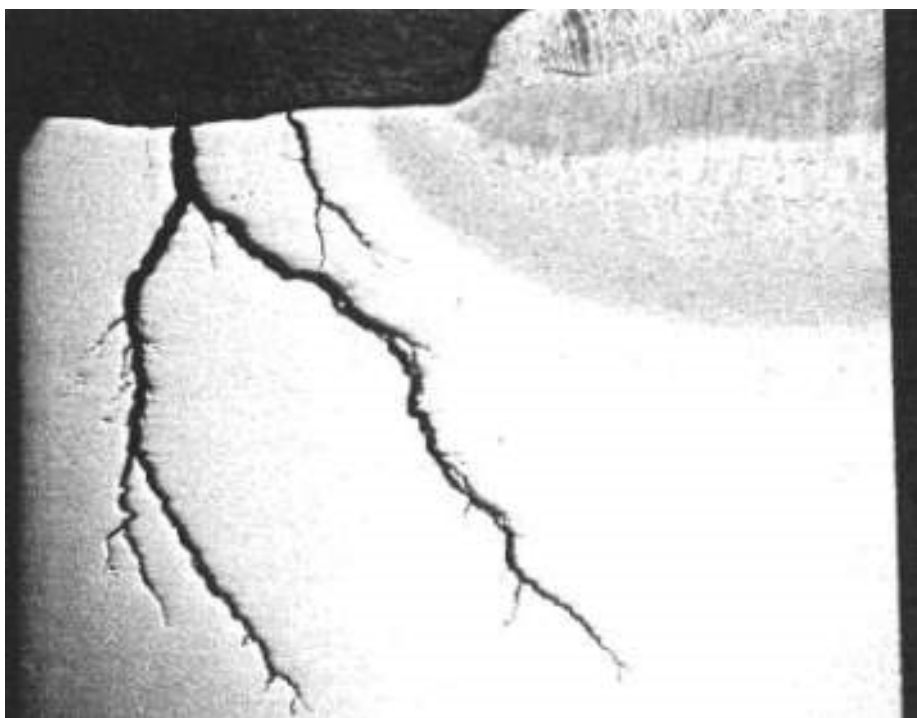


Figure 3-3-1—A photomicrograph of a cross section of a weld in non-PWHT'd carbon steel piping showing amine SCC in the vicinity of a piping weld. Magnification 6X (from API 945).



Figure 3-3-2—Radial amine SCC cracks emanating from the bore of a nozzle in a rich amine reboiler exchanger.

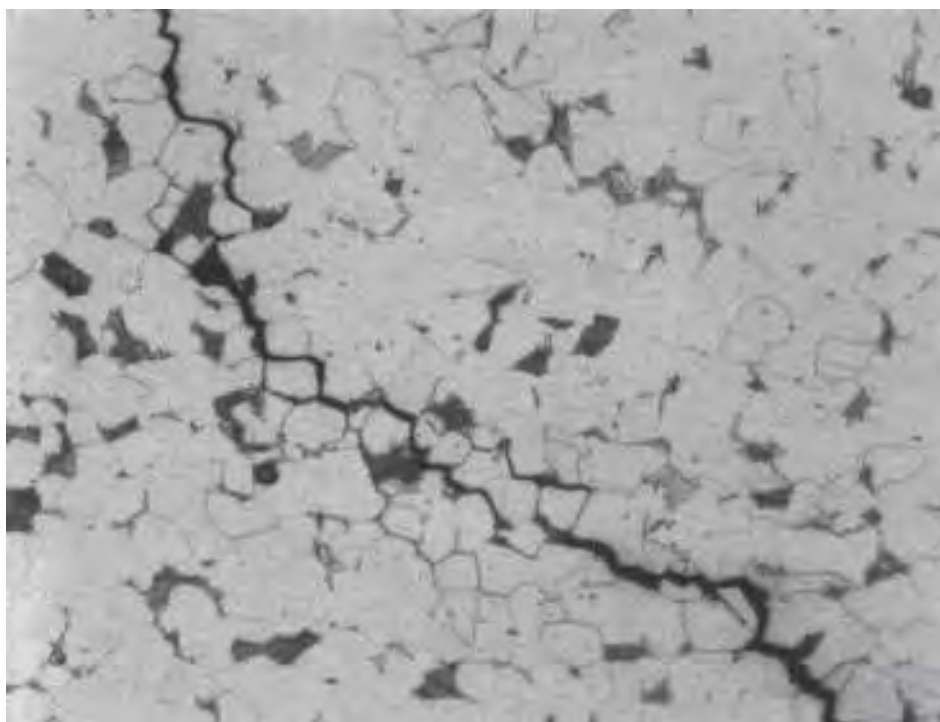


Figure 3-3-3—A higher-magnification view of the crack tip in Figure 3-3-1. Magnification 200X (from API 945).

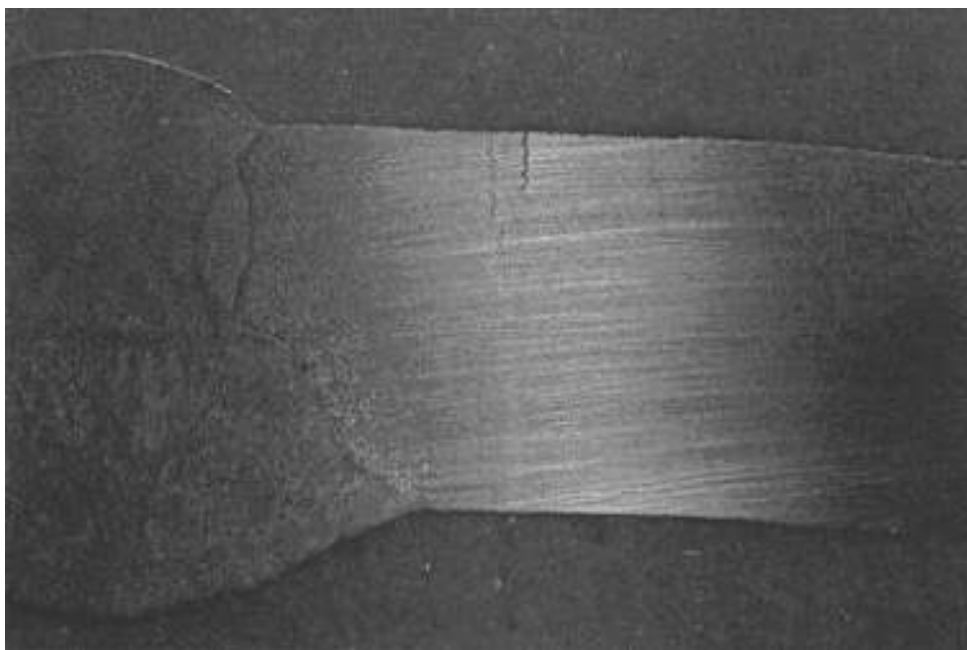


Figure 3-3-4—A photomicrograph of a cross section of a carbon steel piping weld showing amine SCC in a section of the line from the MEA absorber column normally operated at 100 °F (38 °C). Magnification 6X (from API 945).

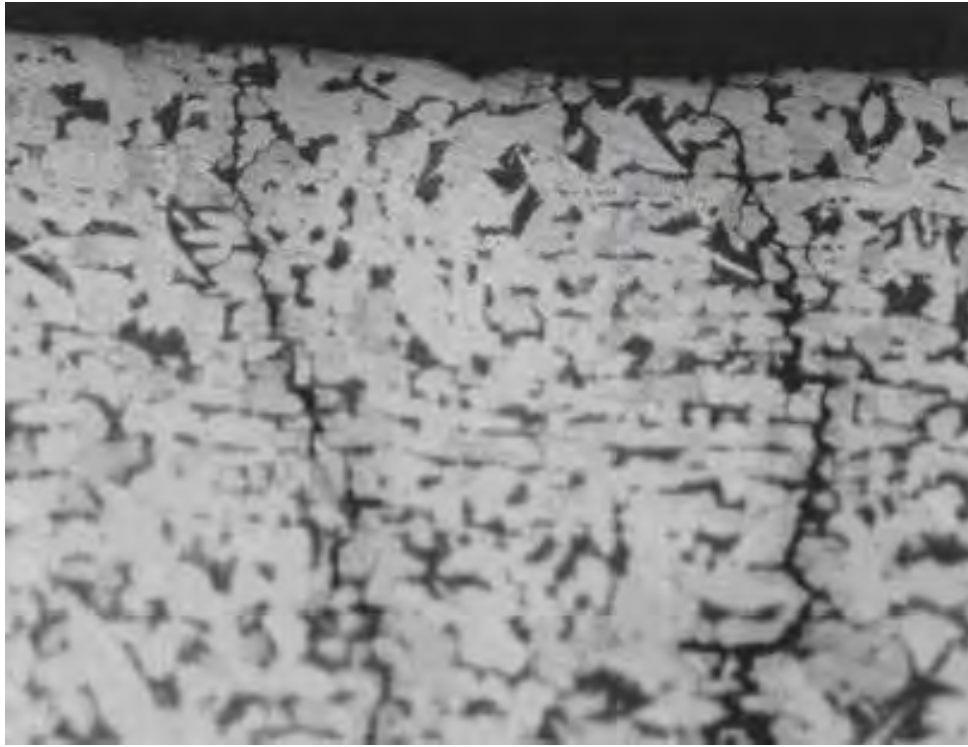


Figure 3-3-5—A higher-magnification view of the cracks in Figure 3-3-4, which illustrates the intergranular nature of the cracking. Magnification 200X (from API 945).

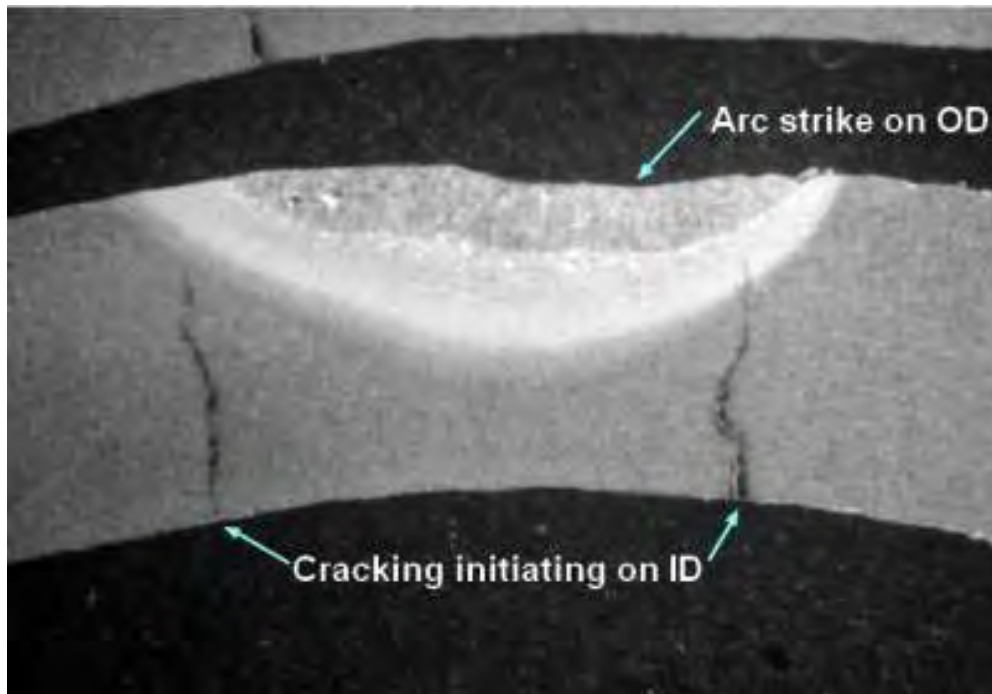


Figure 3-3-6—Amine SCC developed on the inside diameter (ID) beneath an arc strike on the outside diameter (OD) of a 3-in. line in 20 % MEA. The original line was PWHT'd during original fabrication but not the arc strike. Leaks occurred after 30 years of service.

3.4 Ammonia Stress Corrosion Cracking

3.4.1 Description of Damage

- a) Aqueous streams containing ammonia may cause SCC in some copper alloys.
- b) Carbon steel is susceptible to SCC in anhydrous ammonia.

3.4.2 Affected Materials

- a) Copper-zinc alloys (brasses, especially as zinc increases above 15 %), including admiralty brass and aluminum brasses, in environments with aqueous ammonia and/or ammonium compounds.
- b) Carbon steel, especially high-strength steel, in anhydrous ammonia.

3.4.3 Critical Factors

- a) For copper alloys:
 - 1. susceptible alloys may suffer cracking under the combination of residual stress and exposure to ammoniated chemical compounds;
 - 2. zinc content of brasses affects susceptibility, especially as zinc increases above 15 %;
 - 3. a water phase with ammonia or ammoniacal compounds must be present;
 - 4. oxygen is necessary, but trace amounts are sufficient;
 - 5. pH needs to be above 8.5;
 - 6. occurs at any temperature;
 - 7. residual stresses from fabrication or tube rolling are sufficient to promote cracking.
- b) For steel:
 - 1. anhydrous ammonia with < 0.2 % water may cause cracking in carbon steel;
 - 2. cracking has been reported as low as -27 °F (-33 °C) in laboratory testing; crack growth rates and cracking susceptibility increase with increasing temperature, but cracking can occur at ambient or refrigerated conditions;
 - 3. stress relief after welding eliminates susceptibility of most common steels (those not greater than 70 ksi minimum specified tensile strength);
 - 4. contamination with even small amounts of air or oxygen increases tendency toward cracking;
 - 5. high residual stresses from fabrication and welding increase susceptibility.

3.4.4 Affected Units or Equipment

- a) Copper-zinc alloy tubes in heat exchangers.
 - 1. Ammonia is present as a process contaminant in some services or may be intentionally added as an acid neutralizer.
 - 2. Ammonia can be present in cooling water.
 - 3. Ammonia can be present in steam condensate and boiler feedwater (BFW) systems. Some chemicals used for treating BFW, including hydrazine, neutralizing amines, and ammonia-containing compounds, can lead to SCC if not properly controlled.

- b) Non-stress-relieved carbon steel ammonia storage tanks, piping, and equipment in ammonia refrigeration units, as well as some lube oil refining processes.

3.4.5 Appearance or Morphology of Damage

a) Copper alloys.

1. Surface-breaking cracks may show bluish corrosion products.
2. Exchanger tubes show single or highly branched cracks on the surface.
3. Cracking can be either transgranular (Figure 3-4-1 and Figure 3-4-2) or intergranular (Figure 3-4-3), depending on the environment and stress level.

b) Carbon steel.

1. Cracking will occur at exposed non-stress-relieved welds and HAZs.
2. Cracking is primarily intergranular in nature.

3.4.6 Prevention/Mitigation

a) Copper alloys.

1. Copper-zinc alloys with < 15 % zinc have improved resistance.
2. The 90-10 Cu-Ni and 70-30 Cu-Ni alloys have very low susceptibility. Below 120 °F (50 °C), the cupro-nickels are immune for all practical purposes.
3. SCC in steam service can sometimes be controlled by preventing the ingress of air.
4. 300 series SS and nickel-based alloys are immune.

b) Carbon steel.

1. SCC of steel can be prevented through the addition of small quantities of water to the ammonia (0.2 % minimum). Be aware that vapor spaces could have less than 0.2 % water present due to partitioning of ammonia in water phase.
2. An effective stress relief of the welds reduces residual stress to the point where ammonia SCC can be prevented.
3. Low-strength steels (<70 ksi minimum specified tensile strength) should be used.
4. Prevent ingress of oxygen into storage facilities. Even low levels of oxygen (<5 ppm) have been reported to lead to cracking under some conditions. Oxygen levels should be maintained below 1 ppm.
5. Nitrogen can be used to purge oxygen prior to introduction of ammonia into atmospheric and pressurized storage systems.

3.4.7 Inspection and Monitoring

a) For copper alloys:

1. the pH and ammonia content of water draw samples should be monitored to assess susceptibility of copper alloys to determine extent of inspection;
2. heat exchanger tubes can be monitored for cracking using ECT or VT. PT can be applied in the rolled area, which is highly susceptible to cracking.

- b) For carbon steel storage tanks (atmospheric or pressurized), vessels, and piping, in anhydrous ammonia:
1. WFMT is typically used on the welds and HAZs of storage tanks and pressure vessels and can also identify SCC in piping; alternatively, eddy current array testing can be used to perform these inspections;
 2. angle beam UT (SWUT or PAUT) can be performed from the outside surface;
 3. AET can be used for locating cracks and monitoring crack growth in vessels.

NOTE NH_3 SCC can occur parallel, transverse, or oblique to the weld and HAZ. NDE applied should be performed to detect various orientations of SCC.

3.4.8 Related Mechanisms

None.

3.4.9 References

1. *Corrosion Basics—An Introduction*, NACE International, Houston, TX, 1984, p. 117.
2. *ASM Handbook—Corrosion*, Volume 13, ASM International, Materials Park, OH.
3. A. Cohen, "Copper and Copper-base Alloys," *Process Industries Corrosion—The Theory and Practice*, NACE International, Houston, TX, 1986, pp. 479–501.
4. NACE Publication 5A192, *Integrity of Equipment in Anhydrous Ammonia Storage and Handling*, NACE International, Houston, TX, 2004.
5. "Environmental Cracking," Materials Technology Institute, St. Louis, Missouri, 2016.

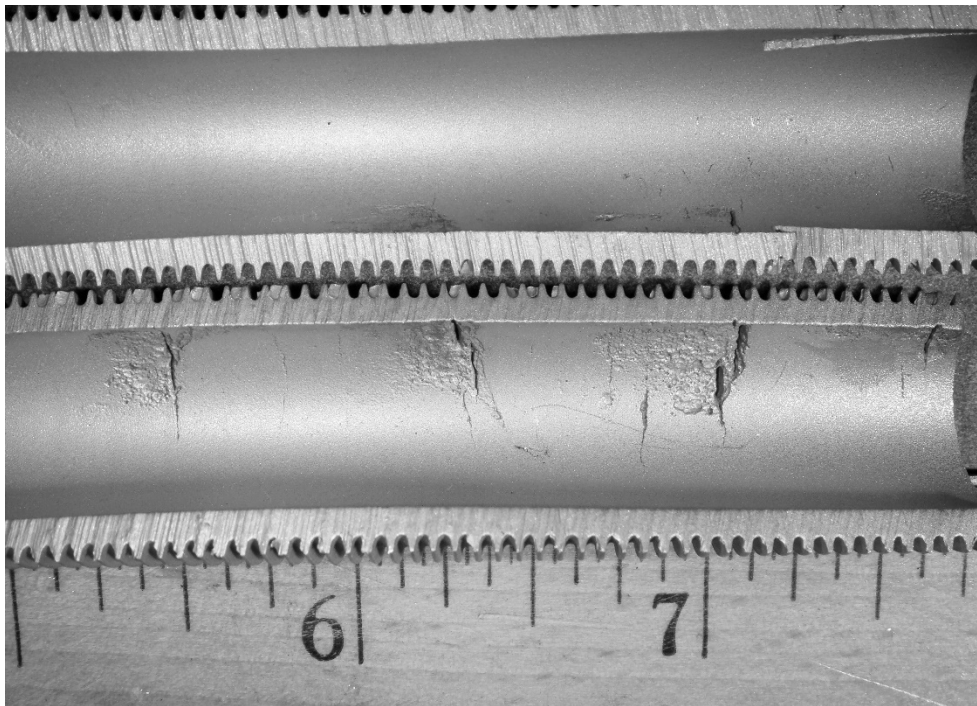


Figure 3-4-1—Ammonia SCC in an inhibited admiralty tube UNS C44300, 0.75 in. diameter, BWG 16 (0.063 in. thick) with extruded fins.

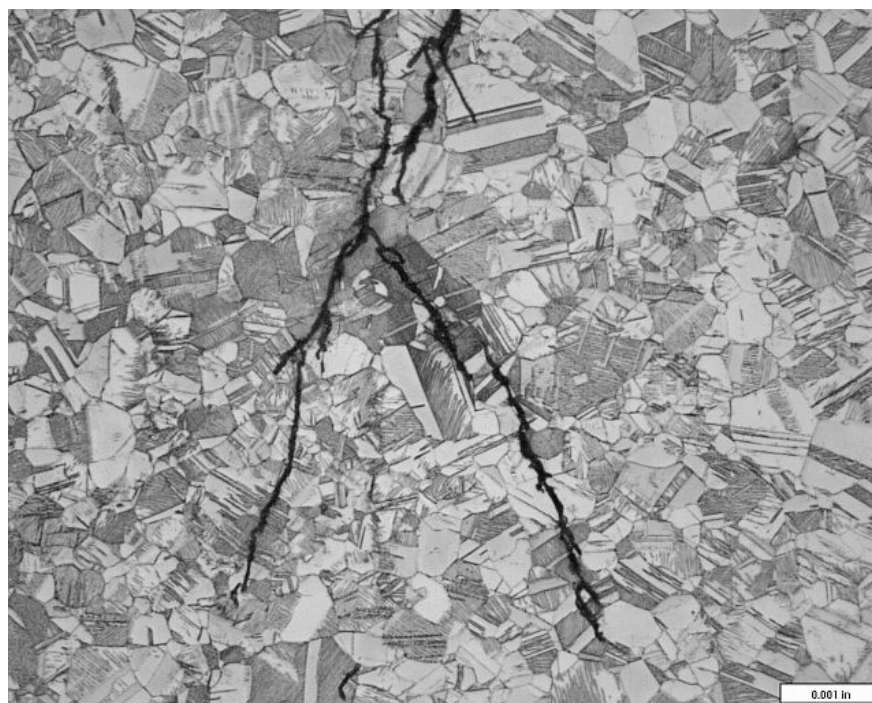


Figure 3-4-2—High-magnification view of a cross section of the tube in Figure 3-4-1 showing transgranular cracking. (Magnification 500X.)

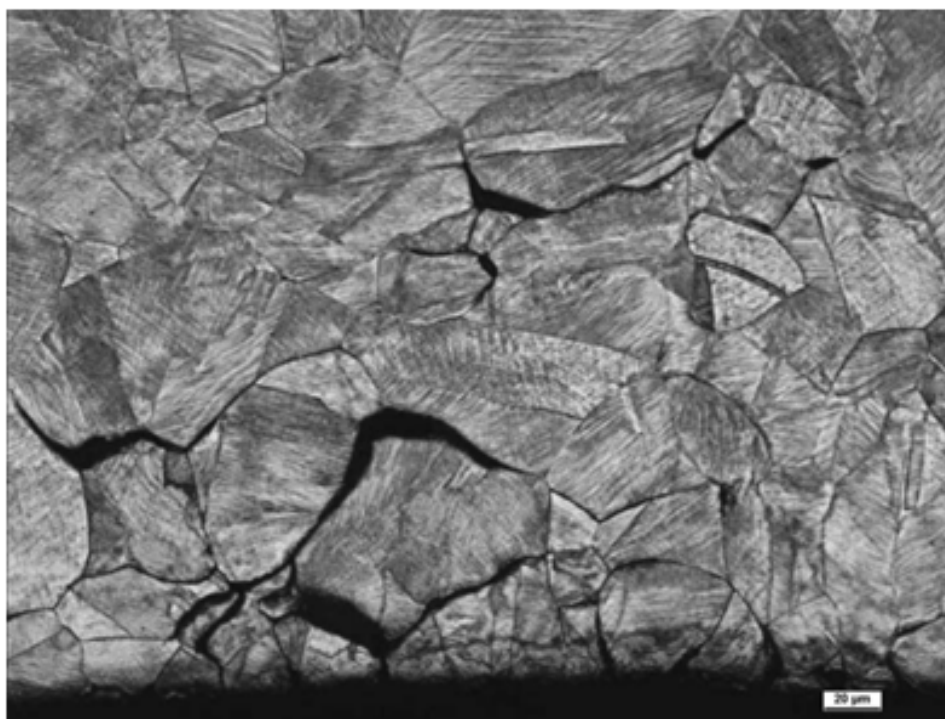


Figure 3-4-3—High-magnification view of a cross section of a brass exchanger tube showing intergranular cracking.

3.5 Ammonium Bisulfide Corrosion (Alkaline Sour Water)

3.5.1 Description of Damage

Aggressive corrosion occurring in hydroprocessing reactor effluent streams and in units handling alkaline sour water (SW), especially in areas of high turbulence.

3.5.2 Affected Materials

- a) Carbon steel and low-alloy steels.
- b) 300 series SS, duplex stainless steel, nickel-based alloys, and titanium and its alloys are more resistant, depending on ammonium bisulfide (NH_4HS) concentration and velocity.
 - 1. Aluminum has been used for NH_4HS corrosion resistance in air coolers, but can suffer high corrosion rates in high-velocity or turbulent locations.
 - 2. Titanium and its alloys have been used for NH_4HS corrosion resistance in air coolers but can suffer embrittlement from hydriding in these services. (See 3.66.)
 - 3. Welds in duplex stainless steel can be susceptible to SSC. (See 3.67 and API 582.)
- c) NH_4HS rapidly corrodes admiralty brass tubes and other copper alloys.

3.5.3 Critical Factors

- a) NH_4HS concentration, H_2S partial pressure, velocity (i.e. wall shear stress), and/or localized turbulence, pH, temperature, alloy composition, and flow distribution are all critical factors to consider.
- b) Corrosion increases with increasing NH_4HS concentration and increasing velocity (i.e. wall shear stress). For carbon steel, solutions below 2 wt % NH_4HS are not generally corrosive. Above 2 wt %, solutions are increasingly corrosive.
- c) In hydroprocessing reactors, nitrogen in the feed is converted to ammonia and reacts with H_2S to form NH_4HS . NH_4HS precipitates out of the gas phase in the reactor effluent stream when temperatures drop to within the range of 120 °F to 150 °F (50 °C to 65 °C), depending on the concentration of NH_3 and H_2S , and may cause fouling and plugging unless flushed away with wash water. A similar reaction between NH_3 and H_2S occurs in FCC and coker units, leading to precipitation in the associated fractionator overheads.
- d) NH_4HS salt deposits can lead to under-deposit corrosion and fouling. The salts are not corrosive unless they become hydrated at which point they become corrosive.
- e) Oxygen and iron in the wash water injected into hydroprocessing reactor effluent can lead to increased corrosion and fouling.
- f) The presence of cyanides increases the severity of corrosion in FCC gas plants, coker gas plants, and sour water stripper (SWS) overheads by diminishing the protection afforded by the normally protective sulfide film.

3.5.4 Affected Units or Equipment

- a) Hydroprocessing units.
 - 1. Several major failures have occurred in hydroprocessing reactor effluent systems due to localized corrosion.
 - 2. Fouling and/or velocity accelerated corrosion may be found at:
 - air cooler header boxes;

- inlet and outlet piping of air coolers;
- exchanger tubes, especially at the inlet and outlet;
- effluent separators and piping into and out of the reactor effluent separators;
- SW draw piping from reactor effluent separators, especially downstream of control valves where flashing may cause severe erosion-corrosion ([Figure 3-5-1](#));
- vapor lines from the high-pressure separator due to entrained or condensed SW;
- hydrocarbon lines from reactor effluent separators due to entrained SW; and
- stripper column overheads containing SW.

b) FCC units.

NH₄HS concentrations are usually less than 2 wt %, but high velocities and/or the presence of cyanides can damage protective iron sulfide scales.

c) SWSs.

High concentrations of NH₄HS and the possible presence of cyanides can lead to corrosion in stripper overhead piping, condensers, and accumulator and reflux piping.

d) Amine units.

High concentrations of NH₄HS may be found in regenerator overheads and reflux piping depending on unit operation.

e) Delayed cokers.

High concentrations of NH₄HS may be found in the gas concentration plant downstream of the fractionator tower.

3.5.5 Appearance or Morphology of Damage

- a) General loss in thickness of carbon steel, with the potential for extremely high localized rates of wall loss at changes in direction or turbulent flow areas above 2 wt % concentration. Generalized corrosion, especially if combined with high unit pressure, can lead to rupture failure.
- b) High localized corrosion rates have also been seen in straight runs of piping, so locating the site of the worst corrosion can be a challenge.
- c) Low velocities may result in extremely localized under-deposit corrosion if sufficient water is not available to dissolve the NH₄HS salts that precipitated.
- d) Heat exchangers may show plugging and loss of duty due to fouling.

3.5.6 Prevention/Mitigation

- a) Good design practice includes symmetrical and hydraulically balanced flow in and out of air-cooled exchangers.
- b) Carefully review design and localized velocities as process conditions change, particularly as NH₄HS concentrations exceed 2 wt % and begin to approach 8 wt % or higher.
- c) Use resistant materials of construction (e.g. duplex stainless steel, Alloy 825) at velocities above 20 fps (6 m/s), depending on NH₄HS concentration.

- d) Properly design and maintain water wash injection with low oxygen content; provide sufficient excess water to ensure that an adequate amount of water remains as liquid to dilute the NH_4HS salts. Use proper injection spray nozzles and metallurgy.
- e) Titanium and Alloy C276 have been used in overhead condensers in SWS units.
- f) Aluminum exchanger tubes are extremely susceptible to erosion-corrosion damage.

3.5.7 Inspection and Monitoring

- a) Ammonium bisulfide corrosion can be highly localized and difficult to locate.
- b) Determine ammonium bisulfide content through sampling or calculation.
- c) UT scanning and/or RT thickness measurement should focus on areas of turbulence and areas of high and low velocity.
 - 1. Special attention should be given to water injection locations in areas of expected water impact (injection point inspection).
 - 2. UT downstream of control valves that see high NH_4HS concentrations.
- d) Permanently mounted thickness monitoring sensors can be used.
- e) Guided wave testing (GWT) can be used as a screening tool.
- f) For steel (magnetic material) air cooler tubes (which are normally finned), internal rotating inspection system (IRIS), magnetic flux leakage (MFL), near-field testing (NFT), and other electromagnetic techniques can be used. ECT and IRIS can be used to inspect nonmagnetic material air cooler tubes.
- g) For steel (magnetic material) exchanger bundle tubes, IRIS, MFL, remote field testing (RFT), and other electromagnetic techniques can be used. ECT and IRIS can be used to inspect nonmagnetic material exchanger bundle tubes.
- h) Water injection facilities and flow meters should be monitored to ensure proper operation. Spray nozzles should be inspected for proper distribution pattern and evidence of damage or distortion.

3.5.8 Related Mechanisms

Erosion/erosion-corrosion (3.27), ammonium chloride corrosion (3.6), concentration cell corrosion (3.19), titanium hydriding (3.66), and chloride SCC (Cl^- SCC) (3.17).

3.5.9 References

1. R.L. Piehl, "Survey of Corrosion in Hydrocracker Effluent Air Coolers," *Materials Protection*, NACE International, Houston, TX, 1976.
2. E.F. Ehmke, "Corrosion Correlation with Ammonia and Hydrogen Sulfide in Air Coolers," *Materials Protection*, NACE International, Houston, TX, 1975.
3. J. Turner, "Control Corrosion in Washwater Systems," *Hydrocarbon Processing*, June 1997, pp. 87–95.
4. C. Harvey and A. Singh, "Mitigate Failures for Reactor Effluent Air Coolers," *Hydrocarbon Processing*, October 1999, pp. 59–72.
5. C.A. Shargay and G.E. Jacobs "Ammonium Salt Corrosion in Hydrotreating Unit Stripper Column Overhead Systems," Paper No. 392, *Corrosion/99*, NACE International, Houston, TX.

6. NACE Publication 34101, *Refinery Injection and Process Mixing Points*, NACE International, Houston, TX, March 2001.
7. API Recommended Practice 932-B, *Design, Materials, Fabrication, Operation, and Inspection Guidelines for Corrosion Control in Hydroprocessing Reactor Effluent Air Cooler (REAC) Systems*, American Petroleum Institute, Washington, DC.
8. C. Shargay and S. Marciniak, "Analyzing Water Washing Requirements for Low Severity Hydroprocessing Units," Paper No. 04646, *Corrosion 2004*, NACE International, Houston, TX.
9. R.J. Horvath, M.S. Cayard, and R.D. Kane, "Prediction and Assessment of Ammonium Bisulfide Corrosion Under Refinery Sour Water Service Conditions," Paper No. 06576, *Corrosion/2006*, NACE International, Houston, TX.
10. H. Iwawaki and K. Toba, "Corrosion Behavior of Steels in Concentrated NH_4HS Environments," Paper No. 07576, *Corrosion 2007*, NACE International, Houston, TX.
11. R.J. Horvath et al., "Prediction and Assessment of Ammonium Bisulfide Corrosion Under Refinery Sour Water Service Conditions—Part 2," Paper No. 10349, *Corrosion/2010*, NACE International, Houston, TX.
12. S. Srinivasan, R.J. Horvath, K.M. Yap, and R.D. Kane, "Prediction and Assessment of Ammonium Bisulfide Corrosion Under Refinery Sour Water Service Conditions—Part 3," Paper No. 08929, *Corrosion/2017*, NACE International, Houston, TX.

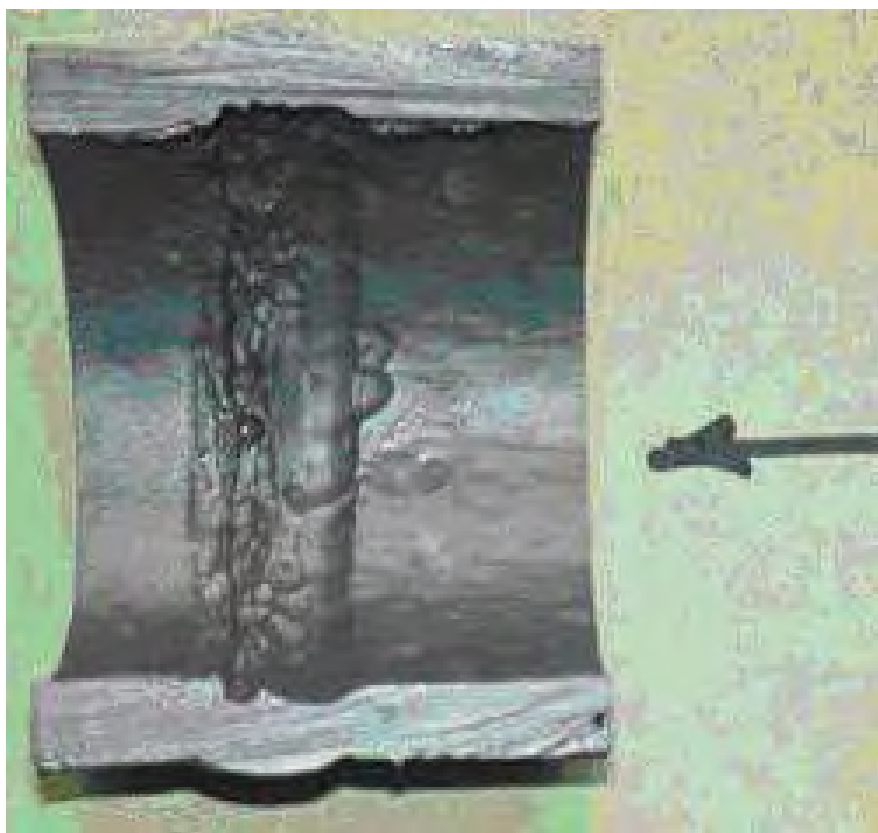


Figure 3-5-1—Ammonium bisulfide corrosion in a 2-in. CS elbow and straight section in a SW line off the cold high-pressure separator (HPS) in an HDT unit.

3.6 Ammonium Chloride and Amine Hydrochloride Corrosion

3.6.1 Description of Damage

Localized corrosion, often pitting, normally occurring under ammonium chloride or amine salt deposits, often in the absence of a free water phase.

3.6.2 Affected Materials

All commonly used materials are susceptible. In order of increasing resistance: carbon steel and low-alloy steels; 300 series SS; duplex stainless steel and Alloys 400, 800, and 825; Alloys 625 and C276; and titanium.

3.6.3 Critical Factors

- a) Concentrations of NH_3 , hydrochloric acid (HCl), and amine salts; temperature; and water availability are the critical factors.
- b) Ammonium chloride salts may precipitate from high-temperature streams as they are cooled, depending upon the concentration of NH_3 and HCl, and may corrode piping and equipment at temperatures well above the water dew point. Salting has been observed up to approximately 400 °F (205 °C).
- c) Ammonium chloride salts are hygroscopic and readily absorb water. A small amount of water can lead to very aggressive corrosion [>100 mpy (>2.5 mm/yr)].
- d) Ammonium chloride is highly water soluble, highly corrosive, and forms an acidic solution when mixed with water. Neutralizing amines can also react with hydrogen chloride to form amine hydrochlorides that can act in a similar fashion.
- e) Corrosion rates increase with increasing temperature.
- f) When the salts deposit above the water dew point, a water wash injection may be required to dissolve them.

3.6.4 Affected Units or Equipment

- a) Crude tower overheads.
 - 1. Tower top, top trays, and overhead piping and exchangers may be subject to fouling and corrosion. Deposits may occur in low-flow zones due to ammonia and/or amine chloride salts condensing from the vapor phase.
 - 2. Top pumparound streams may be affected if ammonia or amine chloride salts are present.
- b) Hydroprocessing.
 - 1. Reactor effluent streams are subject to ammonium chloride salt fouling and corrosion. Water washing may be required if exchanger fouling or loss in duty occurs.
- c) Catalytic reforming.
- d) Reactor effluent streams and the H_2 recycle system are subject to ammonium chloride salting and corrosion.
- e) FCC unit and coker fractionator overheads.
 - 1. Overhead systems and top pumparounds are subject to ammonium chloride corrosion and salting.

3.6.5 Appearance or Morphology of Damage

- a) The salts have a whitish, greenish, or brownish appearance. Water washing and/or steam out will remove deposits so that evidence of fouling may not be evident during an internal VT.
- b) Corrosion underneath the salts is typically very localized and can result in pitting.
- c) Corrosion rates can be extremely high.

3.6.6 Prevention/Mitigation

Alloys that are more pitting resistant will have improved resistance to ammonium chloride salts, but even the most corrosion-resistant nickel-based alloys and titanium alloys may suffer pitting corrosion.

- a) Crude unit.
 - 1. Limit salts by limiting chlorides in the tower feed through desalting and/or the addition of caustic to the desalted crude.
 - 2. A water wash may be required in the crude tower overhead line to flush the salt deposits.
 - 3. Filming amine inhibitors are often added to control corrosion but may not reach metal surfaces under deposits that have already formed.
- b) Hydroprocessing.
 - 1. Limit chlorides in the hydrocarbon feed to the reactor.
 - 2. Limit chlorides in the make-up hydrogen supply.
 - 3. A continuous or intermittent water wash may be required in the reactor effluent stream to flush out the salt deposits or, preferably, prevent them from forming.
 - 4. Monitoring of the feed streams and effluent waters will give an indication of the amount of ammonia and chlorides present; however, process simulation may be required to determine the concentrations and dew point temperatures. If the ammonium chloride salt deposition temperature has been calculated, temperature monitoring and control may be effective for maintaining metal temperatures above the salt deposition temperature.
- c) Catalytic reforming.
 - 1. Net hydrogen produced can be treated in alumina bed chloride traps to remove chlorides.
 - 2. Water washing has been used in some cases, but the system must be carefully designed.
 - 3. Some tower overheads may require neutralizing or filming amines.
- d) FCC and coker units.
 - 1. Continuous water wash in overheads is usually used to dissolve salts as they form.
 - 2. Intermittent water wash can be used to remove salt deposits from fractionator trays. This usually requires "slumping" the column and re-running of affected cuts.

3.6.7 Inspection and Monitoring

- a) Ammonium chloride corrosion can be highly localized and difficult to locate. Salts are often mobile, depending on size of accumulation and hydration, causing them to flow with hydraulic traffic and gravity.

- b) RT or UT scanning methods [automated ultrasonic testing (AUT), manual close-grid, scanning UT] can be used to determine remaining wall thickness. These methods are preferred over typical spot UT thickness monitoring because the corrosion is so highly localized.
- c) GWT can be used as a screening tool.
- d) Permanently mounted thickness monitoring sensors can be used.
- e) Water injection facilities and flow meters should be monitored to ensure proper operation. Spray nozzles should be inspected for proper distribution pattern and evidence of distortion or other damage.
- f) The presence of deposits is often detected when the pressure drop increases or the thermal performance of exchangers has deteriorated.
- g) Corrosion probes or coupons can be useful, but the salt must deposit on the corrosion probe element to detect the corrosion.
- h) For steel (magnetic material) air cooler tubes (which are normally finned), IRIS, MFL, NFT, and other electromagnetic techniques can be used. ECT and IRIS can be used to inspect nonmagnetic material air cooler tubes.
- i) For steel (magnetic material) exchanger bundle tubes, IRIS, MFL, RFT, and other electromagnetic techniques can be used. ECT and IRIS can be used to inspect nonmagnetic material exchanger bundle tubes.

3.6.8 Related Mechanisms

Hydrochloric acid corrosion (3.37), Cl^- SCC (3.17), aqueous organic acid corrosion (3.7), and concentration cell corrosion (3.19).

3.6.9 References

1. C. Shargay et al., "Design Considerations to Minimize Ammonium Chloride Corrosion in Hydrotreater REACs," Paper No. 1543, *Corrosion/2001*, NACE International, Houston, TX.
2. C. Shargay et al., "Ammonium Salt Corrosion in Hydrotreating Unit Stripper Column Overhead Systems," Paper No. 392, *Corrosion/99*, NACE International, Houston, TX.
3. NACE Publication 34101, *Refinery Injection and Process Mixing Points*, NACE International, Houston, TX, March 2001.
4. J. Turner, "Control Corrosion in Washwater Systems," *Hydrocarbon Processing*, June 1997, pp. 87–95.
5. NACE Publication 34105, *Effect of Nonextractable Chlorides on Refinery Corrosion and Fouling*, NACE International, Houston, TX.
6. NACE Publication 34109, *Crude Distillation Unit—Distillation Tower Overhead System Corrosion*, NACE International, Houston, TX, 2009.
7. API Recommended Practice 932-B, *Design, Materials, Fabrication, Operation, and Inspection Guidelines for Corrosion Control in Hydroprocessing Reactor Effluent Air Cooler (REAC) Systems*, American Petroleum Institute, Washington, DC.

3.7 Aqueous Organic Acid Corrosion

3.7.1 Description of Damage

Organic compounds present in some crude oils decompose in the crude furnace to form low molecular weight organic acids (Table 3-7-1) that are soluble in water. They may also result from additives used in upstream operations or desalting. These acids can contribute significantly to aqueous corrosion depending on the type and quantity of acids and the presence of other contaminants, particularly if they condense in distillation tower overhead systems. They can also cause corrosion at mix points where recovered oil streams are injected.

3.7.2 Affected Materials

- a) Carbon steel and low-alloy steels are affected.
- b) Most corrosion-resistant alloys used in crude tower overhead systems are generally not affected.
 - 1. Austenitic stainless steels are generally resistant, but this mechanism is often associated with streams that cause inorganic acid corrosion as well as pitting and SCC due to halogens (e.g. chlorides), so their use should be avoided unless it is known that halogens are not present.

3.7.3 Critical Factors

- a) Corrosion is a function of the type and quantity of organic acids, metal temperature, fluid velocity, system pH, and presence of other acids.
- b) The low-molecular-weight organic acids that are formed include formic acid, acetic acid, propionic acid, and butyric acid.
- c) The lower-molecular-weight acids such as formic acid and acetic acid are the most corrosive. They are soluble in naphtha and are extracted into the water phase, once the water condenses, and contribute to a reduction of pH.
- d) The presence of organic acids will contribute to the overall demand for neutralizing chemicals, but their effects may be completely masked by the presence of other acids such as HCl, H₂S, carbonic acid, and others.
- e) Corrosion is most likely to be a problem where relatively “non-corrosive” conditions have existed in an overhead system. When there is a sudden increase in low molecular weight organic acids, it can reduce the pH of the water in the overhead system and cause a potentially unexpected increase in neutralizer demand.
- f) The type and quantity of organic acids formed in the overhead system are crude specific. One source of these acids is believed to be the thermal decomposition of naphthenic acids in the crude, which may be precursors to light organic acid formation. In that case, the processing of higher total acid number (TAN) crudes might increase organic acid in the overheads. However, very little published information is available on this subject.
- g) Some higher molecular weight organic acids condense above the water dew point in overhead systems, but they are generally not present in sufficient quantities to cause corrosion.
- h) Light organic acids such as acetic acid are sometimes added during oilfield operations, e.g. in dehydrators or desalters to improve performance and inhibit calcium naphthenate salt deposition. (Reference 2) Such acids will vaporize in the crude preheat exchangers and furnace and go up the column into the crude tower overhead system.
- i) Other, high molecular weight acids used as oilfield additives can thermally decompose at crude unit temperatures to form volatile, corrosive light organic acids such as acetic and formic acids.
- j) In general, light organic acids do not generate the severity of corrosion associated with inorganic acids such as HCl. Table 3-7-1 shows the HCl equivalent factor for corrosion by organic acids in overhead systems. To calculate the HCl equivalent of an organic acid, multiply the content of the organic acid (in weight ppm) by the factor for that acid, and the result will be the equivalent content of HCl (in ppmw). This number can then be used to estimate the additional neutralizer needed in the overhead system to compensate for the organic acids present. This must be done with caution, because excess neutralizer can lead to amine hydrochloride salts in overhead systems.

3.7.4 Affected Units or Equipment

- a) All carbon steel piping and process equipment in crude tower, vacuum tower, visbreaker, and coker fractionator overhead systems including heat exchangers, towers, and drums are susceptible to corrosion where acidic conditions occur.
- b) Localized corrosion can occur at mix points from recovered oil streams when wet streams combine with streams contaminated with organic acid.
- c) Corrosion tends to occur where water accumulates or where hydrocarbon flow directs water droplets against metal surfaces. Examples include the bottoms of overhead separator drums and exchanger shells or channels, the boots of separator drums, and liquid hold-up areas on trays.
- d) In horizontal piping, organic acid corrosion is generally found both in the vapor space where liquid water can condense and along the bottom of the piping where liquid water may run.
- e) Corrosion is also sensitive to flow rate and will tend to be more severe in higher-velocity and turbulent areas in piping systems such as elbows, tees, downstream of pumps, and downstream of control valves. Other areas of potentially more severe corrosion due to velocity and turbulence include overhead transfer lines, overhead condensers and separator drums, and exchanger tubes.

3.7.5 Appearance or Morphology of Damage

- a) Aqueous organic acid corrosion will result in thinning. General and local wall loss can be expected. In carbon steels, local losses are observed where a water phase is being formed such as during condensation or separation.
- b) Light organic acid corrosion typically leaves the corroded surface smooth and damage may be difficult to distinguish from corrosion by other acids in the overhead system. It is sometimes mistaken for HCl corrosion or carbonic acid (CO_2) corrosion.
- c) In pipe or other equipment where there is significant flow, the surfaces are sometimes smoothly grooved.
- d) Localized pitting occurs in low-velocity or condensing conditions.

3.7.6 Prevention/Mitigation

- a) Corrosion caused by light organic acids in crude unit overhead systems can be minimized through the injection of an acid-neutralizing additive. However, problems may arise when frequent changes in crude blends lead to frequent changes in neutralizer demand.
- b) The TAN of the crudes being processed can be used as an initial guide to determine the neutralizer requirement. If the crude TAN increases, one should anticipate an increase in the acid concentration in the overhead system.
- c) After a new crude is processed, a review of analyses of water samples from the boot of the overhead separator drum can be used to determine how much light organic acid reaches the overhead system and thereby optimize future neutralizer additions.
- d) Filming amines can also be used to prevent corrosion if the filming amine selected does not react with the organic acid. However, filming amines are generally not as effective as neutralization in mitigating overhead system corrosion.
- e) Upgrading to corrosion-resistant alloys will prevent organic acid corrosion, but the selection of suitable materials should account for other potential damage mechanisms in the overhead system.

3.7.7 Inspection and Monitoring

- a) Various UT and RT techniques can be used to assess metal loss.
- b) GWT and electromagnetic acoustic transducer (EMAT) can be utilized to screen for wall loss.
- c) Corrosion probes and corrosion coupons have proven valuable, especially in conjunction with water sample analysis.
- d) Permanently mounted thickness monitoring sensors can be used.
- e) Infrared thermography scanning can also be used to detect locations where liquid water may exist and in this way supplement other NDE methods.
- f) The pH should be monitored where water is known to accumulate in the process, particularly at the overhead accumulation drum of the crude tower. If a low pH is found that cannot be accounted for by the level of chlorides measured, additional acids, potentially including organic acids, are likely present.

3.7.8 Related Mechanisms

HCl corrosion (3.37) and naphthenic acid corrosion (NAC) (3.46).

3.7.9 References

1. R.R. Petersen, "Improve Corrosion Control by Computer Simulation," *Hydrocarbon Processing*, January 1992, pp. 50–55.
2. S. Kapusta, F. van den Berg, R. Daane, and M.C. Place, "The Impact of Oil Field Chemicals on Refinery Corrosion Problems," Paper No. 03649, *Corrosion/2003*, NACE International, Houston, TX.
3. S. Lordo, J.M. Garcia, and S. Garcia-Swofford, "Desalter Acidification Additives and Their Potential Impacts on Crude Units," Paper No. 08556, *Corrosion/2008*, NACE International, Houston, TX.
4. R. Sharpe et al., "Crude Unit Overhead Corrosion Control," Paper No. 98585, *Corrosion/98*, NACE International, Houston, TX.
5. NACE Publication 34109, *Crude Distillation Unit—Distillation Tower Overhead System Corrosion*, NACE International, Houston, TX, 2009.
6. J.R. Rue and D.P. Naeger, "Advances in Crude Unit Corrosion Control," Paper No. 87199, *Corrosion/87*, NACE International, Houston, TX.
7. NACE Publication 34105, *Effect of Nonextractable Chlorides on Refinery Corrosion and Fouling*, NACE International, Houston, TX.

Table 3-7-1—Light Organic Acid Corrosion Equivalency Factors

Acid	HCl Equivalent Factor
Formic	0.76
Acetic	0.61
Propionic	0.49
Methyl propionic	0.41
Butanoic	0.41
3-methyl butanoic	0.36
Pentanoic	0.36
Hexanoic	0.31
Heptanoic	0.28

3.8 Atmospheric Corrosion

3.8.1 Description of Damage

Corrosion that occurs from moisture associated with atmospheric conditions. Marine environments and moist, polluted industrial environments with airborne contaminants are the most severe. Dry rural environments cause very little corrosion.

3.8.2 Affected Materials

Carbon steel, low-alloy steels, and copper alloyed aluminum.

3.8.3 Critical Factors

- a) The physical location of the plant (industrial, marine, urban, rural).
- b) The amount of moisture (humidity, rainfall) typically present or the presence of cooling tower mist.
- c) The presence of salts, sulfur compounds, dirt, or other contaminants in the air.
- d) Chlorides, H₂S, fly ash, and other airborne contaminants from cooling tower and wet gas scrubber drift, furnace stacks, and other equipment accelerate corrosion.
- e) Orientation to the prevailing wind and rain.
- f) Corrosion rates increase with temperature up to about 250 °F (120 °C). Above 250 °F (120 °C), surfaces are usually too dry for corrosion to occur except under insulation. (See [3.22.](#))
- g) Designs that trap water or moisture in crevices or other configurations are more prone to attack.
- h) Marine environments can be very corrosive (about 20 mpy) as are industrial environments that contain acids or sulfur compounds that can form acids (about 5 mpy to 10 mpy).
- i) Inland locations exposed to a moderate amount of precipitation or humidity are considered moderately corrosive environments (about 1 mpy to 3 mpy).
- j) Dry rural environments usually have very low corrosion rates (<1 mpy).
- k) Bird droppings can also cause accelerated corrosion and unsightly stains.

3.8.4 Affected Units or Equipment

- a) Unpainted, uninsulated carbon steel and low-alloy steel piping and equipment operating below 250 °F (120 °C) where moisture can contact the surface.
- b) Uninsulated carbon and low-alloy steel equipment with deteriorated paint/coating.
- c) Equipment downwind of cooling towers and wet gas scrubbers.
- d) Equipment may be susceptible if cycled between ambient and higher or lower operating temperatures.
- e) Equipment shut down or idled for prolonged periods unless properly mothballed.
- f) Tanks and piping are particularly susceptible. Piping that rests on pipe supports is very prone to attack due to water entrapment between the pipe and the support.
- g) Piers and docks are very prone to attack from the marine environment.

- h) Bimetallic connections such as copper to aluminum electrical connections.

3.8.5 Appearance or Morphology of Damage

- a) The attack will be general or localized, depending upon the condition of the coating, if any, and whether or not the moisture is trapped.
- b) If there is no coating, corrosion or loss in thickness can be more general and widespread.
- c) Localized coating failures will promote localized corrosion.
- d) Metal loss may not be visually evident, although normally a distinctive iron oxide (red rust) scale forms as shown in [Figure 3-8-1](#).

3.8.6 Prevention/Mitigation

Paints or coatings are normally applied to otherwise unprotected equipment to prevent atmospheric corrosion. Surface preparation and proper coating application are critical for long-term protection in corrosive environments.

3.8.7 Inspection and Monitoring

- a) VT includes direct/line-of-sight and indirect methods using a camera, mirror, laser scanning, and/or structured white light imaging with pit gages.
- b) UT can include techniques like straight beam or angle beam (SWUT or PAUT) to directly measure remaining wall thickness or screening techniques using EMAT or GWT.
- c) RT may include traditional (film based), digital, or computed radiography media and may incorporate techniques such as contact or profile RT as well as open system imaging.
- d) ECT may include a screening technique such as pulsed eddy current (PEC).

3.8.8 Related Mechanisms

Corrosion under insulation (CUI) ([3.22](#)) and concentration cell (touch point) corrosion ([3.19](#)).

3.8.9 References

1. *ASM Handbook—Corrosion*, Volume 13, ASM International, Materials Park, OH.



Figure 3-8-1—Atmospheric corrosion of an LPG line in close proximity to a cooling tower.

3.9 Boiler Water and Steam Condensate Corrosion

3.9.1 Description of Damage

General corrosion and pitting in the boiler system and condensate return system. It is primarily the result of dissolved oxygen and/or carbon dioxide, which could lead to oxygen pitting corrosion and carbonic acid corrosion, respectively. Flow accelerated corrosion (FAC) in these systems may occur either as general wall thinning corrosion or localized corrosion at high velocity, high turbulence, or change of flow direction locations.

3.9.2 Affected Materials

Carbon steel and low-alloy steels.

3.9.3 Critical Factors

- a) Critical factors are the concentration of dissolved gas (oxygen and/or carbon dioxide), pH, temperature, quality of the feedwater, and the specific feedwater treating system.
- b) Corrosion protection in the boiler is accomplished by laying down and continuously maintaining a layer of protective Fe_3O_4 (magnetite).
- c) In the case of FAC, this protective oxide layer is dissolved or prevented from forming. Carbon steel is the most affected. Alloying elements in low-alloy steels such as Cr, Cu, and Mo can enhance corrosion resistance. The most critical temperature for FAC is 300 °F (150 °C), and it decreases with increasing pH. Too low an oxygen concentration increases the corrosion due to the inability to form the protective oxide layer. At least 3 ppb to 7 ppb may be required to form the oxide layer.
- d) The chemical treatment for scale and deposit control must be adjusted to coordinate with the oxygen scavenger for the specific water service and BFW treating system.
- e) Oxygen pitting can occur if the deaeration and oxygen scavenging treatment are not working correctly.

3.9.4 Affected Units or Equipment

- a) Corrosion can occur throughout the boiler water treatment system, including the deaerating equipment, feedwater lines, and pumps, as well as in the steam generation system including stage heaters, economizers, and boiler tubes as well as process unit steam generators.
- b) Corrosion in the condensate return system as well as in process unit reboilers and associated piping may be due to carbon dioxide, although oxygen pitting from oxygen contamination is also possible as well as FAC if the proper conditions are present.
- c) Threaded connections are especially susceptible.

3.9.5 Appearance or Morphology of Damage

- a) Corrosion from oxygen is normally a pitting type damage. It can occur anywhere in the system there is in-leakage of air or even if only very small quantities break through the oxygen scavenging treatment. Oxygen is particularly aggressive in equipment such as closed heaters and economizers where there is a rapid water temperature rise. (Figure 3-9-1)
- b) Carbon dioxide corrosion is normally smooth, but it can also cause grooving of the pipe wall. (Figure 3-9-2)
- c) Corrosion may be localized at areas where gases in the water are most concentrated, such as at the water to vapor interface level in a vertical reboiler.
- d) FAC failures are often located in areas where there is a flow disturbance such as an orifice run, flow meter, elbow, reducer, or other types of fittings. The wall thinning occurs just downstream of these flow disturbances,

leaving behind a corroded surface free of oxide scale, sometimes with a specific flow pattern. FAC has led to rupture of piping.

3.9.6 Prevention/Mitigation

- a) Oxygen removal from BFW typically includes mechanical deaeration followed by scavenging with catalyzed sodium sulfite or hydrazine, depending on the system pressure level. Proper deaerator operation and accurately controlled scavenger chemical addition are important. A residual of the oxygen scavenger is carried into the steam generation system to handle any oxygen ingress beyond the deaerator.
- b) If the scale and deposit control along with the magnetite maintenance treatment scheme do not minimize carbon dioxide corrosion in the condensate return system, an amine inhibitor treatment might be required.
- c) Boiler water needs to be blown down to control the concentration of solids and non-condensable gases. Steam equipment should be checked to ensure there are working non-condensable vents. It is also important that steam piping and equipment allow for blowdown of condensation (e.g. using steam traps and functional mechanical steam separation devices like coalescers).
- d) Water treatment, sampling, and analysis are the common methods used to ensure integrity and prevent boiler water and condensate corrosion.
 - 1. It may be necessary to modify or improve the water treatment program if problems such as a ruptured boiler tube or condensate leaks occur in the boiler water or condensate systems.
- e) The pH, temperature, and oxygen concentration are the main parameters that can affect the potential for FAC. BFW pH from 9.2 to 9.6 is often recommended. Upgrading the material to Cr-Mo steel usually solves the problem.
 - 1. Too low or total absence of oxygen is no longer considered the best corrosion control for BFW and condensate. Oxygenated treatments that deliberately inject oxygen into the condensate and BFW system or the use of oxygen scavenger at reduced concentrations may be necessary to maintain oxygen levels within the desired range to mitigate FAC.

3.9.7 Inspection and Monitoring

- a) Monitoring the appropriate parameters can indicate whether the treatment program is performing satisfactorily.
 - 1. Parameters that can be monitored through analysis include pH, alkalinity, hardness, conductivity, chlorine or residual biocide, dissolved gases (oxygen and carbon dioxide), iron, copper, and total dissolved solids
- b) Vacuum testing can be used to check for air ingress into the condenser hotwell.
- c) UT and RT methods can be used to monitor for pipe wall thinning.
- d) For boilers, there are no practical online inspection methods.
 - 1. UT and RT can be performed on boiler tubes and other boiler components when the system is offline.

3.9.8 Related Mechanisms

CO₂ corrosion (3.18), corrosion fatigue (3.21), erosion/erosion-corrosion (3.27), oxygenated water corrosion (3.49), and ammonia SCC of copper alloys (3.4).

3.9.9 References

- 1. *Betz Handbook of Industrial Water Conditioning*, Eighth Edition, Betz Laboratories, Trevose, PA, 1980.

2. R.D. Port and H.M. Herro, *The Nalco Guide to Boiler Failure Analysis*, McGraw-Hill, New York, NY, 1991.
3. NACE SP0590, *Prevention, Detection, and Correction of Deaerator Cracking*, NACE International, Houston, TX.
4. T.Y. Chen et al., "Condensate Corrosion in Steam Generating Systems," Paper No. 98718, *Corrosion/98*, NACE International, Houston, TX.
5. R.B. Dooley and V.K. Chexal, "Flow-accelerated Corrosion," Paper No. 99347, *Corrosion/99*, NACE International, Houston, TX.
6. Nuclear Safety NEW/CSNI/R(2014), CODAP Topical Report: "Flow Accelerated Corrosion (FAC) of Carbon Steel and Low Alloy Steel Piping in Commercial Nuclear Power Plants," <https://www.oecd-neo.org/nsd/docs/2014/csni-r2014-6.pdf>, June 2014.

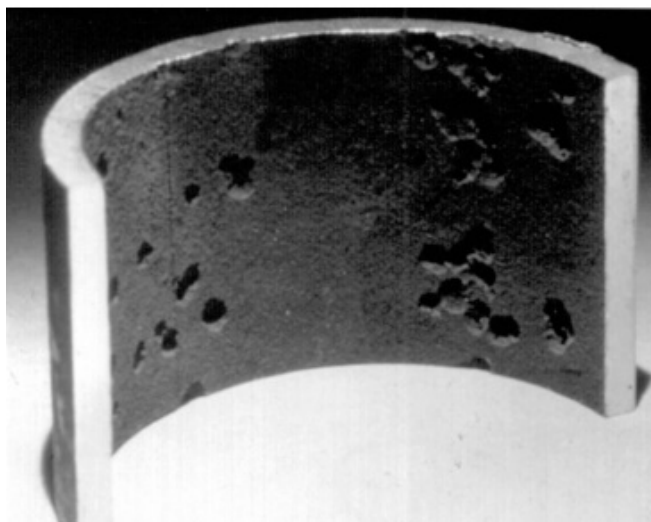


Figure 3-9-1—Pits caused by oxygen corrosion.

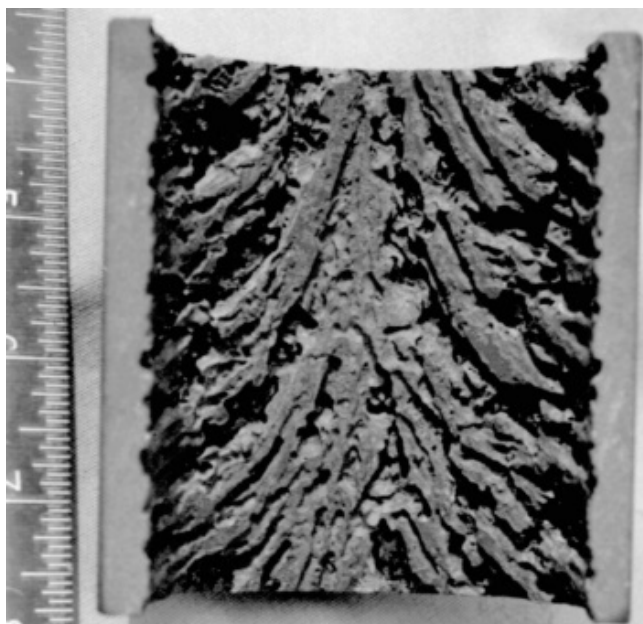


Figure 3-9-2—Jagged fir-tree pattern of corrosion inside a tilted steel pipe caused by condensing steam containing high concentrations of carbon dioxide.

3.10 Brine Corrosion

3.10.1 Description of Damage

- a) Widespread or localized pitting occurring on the surface of equipment exposed to aqueous solutions of dissolved salts, typically a chloride or other halide salt. This mechanism is often present with other mechanisms such as oxygen corrosion, galvanic corrosion, and microbiologically influenced corrosion (MIC).
- b) In chloride brine corrosion of stainless steels, pits are initiated where chlorides break down the passive layer. Once the pit is initiated, chlorides migrate within the pit, hydrolyze to an acidic species, decrease the pH in the pit, and further accelerate corrosion by this autocatalytic process. A similar process occurs in crevices. Additionally, other anions like nitrates and sulfates hydrolyze within pits and crevices to drive the pH down, but these are less mobile than chlorides so their effect is less significant.

3.10.2 Affected Materials

- a) Carbon steel, alloy steel, or stainless steel, with carbon steel being the most common material exposed to brine solutions. Aluminum alloys are also susceptible to brine corrosion. Ni-Cr-Mo alloys have improved resistance to brine corrosion.
- b) Copper alloys are generally more resistant to pitting in brine solutions than stainless steel and carbon steel, but the tenacity of the protective film is affected by other contaminants in the stream, including sulfides and ammonia.
- c) Resistance of specific alloys is complicated by other concurrent damage mechanisms. For example, oxygen corrosion or under deposit corrosion can be active, with the brine solution chemistry contributing to these mechanisms.
- d) Fiber reinforced plastic (FRP) piping is immune to this damage mechanism.

3.10.3 Critical Factors

- a) Concentration of dissolved salt, oxygen concentration, pH, velocity, and temperature are the critical factors.
- b) Corrosion rates increase with increasing temperature.
- c) Corrosion rates increase with increasing oxygen content.
- d) Corrosion rates typically increase with decreasing pH, the corrosion becoming more aggressive in more acidic solutions. Decreasing pH also increases pitting and crevice corrosion rates of stainless steels due to the passive layer being less stable at lower pH.
- e) Corrosion rates increase with increasing salt content. For stainless steels and related alloys, increasing concentration of halides reduces the critical pitting temperature and critical crevice corrosion temperature for a given alloy.
- f) The type of salt species present will affect the corrosion rate. Chlorides are the most common cause of corrosion in brine solutions, but other halides, e.g., bromides can also cause corrosion. Chlorides, sulfates, and nitrates contribute to oxygen corrosion of carbon steel by migrating into oxygen corrosion pits, hydrolyzing to form acidic ions, and decreasing the pH under a tubercle.
- g) High velocity can contribute to erosion-corrosion, especially if particulates are present. However, stagnant conditions can also exacerbate corrosion by allowing accumulation of deposits. Copper-alloys and carbon steel tend to be more susceptible to erosion-corrosion than stainless steel.
- h) The chloride pitting and crevice corrosion resistance of stainless steels and higher alloy Fe-Ni-Cr alloys is quantified by the Pitting Resistance Equivalent Number (PREN).

1. $PREN = \%Cr + 3.3 \times (\%Mo + 0.5 \times \%W) + 16 \times \%N$
 2. Generally, a PREN of 40 or higher is considered necessary to resist corrosion in aerated seawater in ambient conditions. In stainless steels, an increase in molybdenum content improves resistance to chloride pitting and crevice corrosion in brine solutions, as can be seen by the increase in PREN. Nitrogen additions are also very potent in increasing resistance.
 3. Chloride pitting penetration rates can be worse in stainless steels with a low PREN than in carbon steel due to the cathodic potential provided by the passive layer around the pit in driving the pitting corrosion process as well as the nature of the autocatalytic acid chloride hydrolysis mechanism of chloride pitting in stainless steel.
- i) The presence of free chlorine above approximately 0.5 ppm (e.g. biocide treatment in seawater systems) increases seawater corrosion rates of carbon steel and stainless steel, in both stagnant and flowing conditions.
 - j) The presence of sulfur-containing compounds can reduce the corrosion resistance of copper-based alloys by changing the passivity of the protective surface film.
 - k) The presence of hydrogen sulfide can accelerate attack. H_2S ionizes in the brine solution to form an acid that reacts with steel to form loose, porous, non-protective iron sulfide deposits on the pipe surface.
 - l) The use of free-machining stainless steel can initiate pitting more rapidly.

3.10.4 Affected Units or Equipment

- a) Crude distillation unit desalters and desalter effluent systems.
- b) Effluent water treatment systems. High corrosion rates are commonly observed in transfer lines between ponds, outlet piping of brine separators, and piping in intermittent service. (Figures 3-10-1 and 3-10-2)
- c) Salt driers for water removal from final product.
- d) Seawater systems (e.g. firewater).
- e) Water softener regeneration systems.

3.10.5 Appearance or Morphology of Damage

- a) Carbon Steel - Heavy scaling and possible tubercles since the mechanism is typically a result of chlorides or other anions accelerating oxygen pitting. Removal of the scale reveals under-deposit type corrosion and large, wide pits, with corrosion rates observed up to 60 mpy.
 1. Where sulfate reducing bacteria (SRB) are present, severe pitting/channeling can occur along the top or bottom of the pipe.
 2. Preferential corrosion in welds and heat affected zones sometimes occurs in carbon steel.
- b) Stainless Steel – Sharp, deep, isolated pits are typical of chloride pitting and crevice corrosion of stainless steel. Chloride SCC is also possible, depending on the temperature. (See 3.17.)

3.10.6 Prevention/Mitigation

- a) Sources of dissolved oxygen should be identified and eliminated. A deaerated water source should be used for desalter wash water make-up. Accidental aeration can be corrected through improved design or water treatments such as vacuum deaeration or chemical scavenging. An effective scavenger in brine systems is sodium metabisulfite. Water is oxygenated during movement in and out of ponds, especially where it freefalls. O_2 content should be checked downstream of the brine separator and discharge of pumps.

- b) Heat exchangers should be operated to prevent vaporization or precipitation of deposits.
- c) Low residual chlorine levels should be maintained when treating for prevention of MIC (< 0.5 ppm for carbon steel, 0.7-5 ppm for super duplex systems depending on temperature, and < 5 ppm for Cu-Ni). Bacteria which can contribute to microbiologically influenced corrosion should be monitored. (See 3.45.) Typical locations to monitor for SRB are inlets and outlets to fresh water rivers, canals, or ponds.
- d) Upgrading to a more corrosion resistant alloy such as a Ni-Cr-Mo alloy or to a non-metallic such as FRP or polyvinyl chloride (PVC) can help mitigate corrosion. FRP is immune and has been the modern material of choice. However, there are limitations on operating pressures and temperatures that can impact the ability to meet design and cost constraints.
- e) Internal coatings can provide some protection to carbon steel for this type of service. Epoxy phenolic and coal tar epoxy coatings have been used as well as polypropylene-lined pipe. However, care must be taken to avoid galvanic coupling with more noble materials. (See 3.31.) Also, the coating integrity must be well maintained to prevent creating an aeration cell next to voids.

3.10.7 Inspection and Monitoring

- a) UT, including UT scanning, can be used for external, opposite side thickness measurements. RT can also be used where pipe dimensions allow.
- b) GWT can be used for screening long pipe runs to identify areas for local follow-up measurements, but it may not detect isolated pitting.
- c) Corrosion coupons or electric resistance probes can assist in determining short & long-term corrosion rates. The coupons also provide a visual indication of the damage mode present in the system.
- d) Dissolved O₂ content should be monitored.
- e) Permanently-mounted thickness monitoring sensors can be used.

3.10.8 Related Mechanisms

Microbiologically influenced corrosion (3.45), erosion/erosion-corrosion (See 3.27), chloride stress corrosion cracking (See 3.17), cooling water corrosion (3.20), galvanic corrosion (3.31), concentration cell corrosion (3.19), and oxygenated water corrosion (3.49).

3.10.9 References

1. D. A. Jones, "Principles and Prevention of Corrosion," 2nd edition, Prentice-Hall, Inc, 1996.
2. H. M. Herro, R. D. Port, "The Nalco Guide to Cooling Water System Failure Analysis," McGraw-Hill Inc, 1993.
3. "Evaluation of In-Line Corrosion Coupons," R. W Elliot, Ortech Corporation, September 1998. Paper No. 98-J41-M0201.
4. W. Schleich, "Selection of Material for Seawater Piping Systems," KME Germany AG, Rev. 2008
5. NORSOK Standard M-001, Materials Selection, Rev. 3, Nov. 2002.
6. S. A. Silverman, et. al., "Use of High-Strength Alloys and Elastomers in Heavy Completion Brines," SPE 84515, SPE Annual Technical Conference and Exhibition in Denver, Colorado, USA, 8 October 2003, Society of Petroleum Engineers, Inc.
7. J. W. Oldfield, G. L. Swales, B. Todd, "Corrosion of Metals in Deaerated Seawater," Proceedings of the Second BSE-NACE Corrosion Conference, January 19–21, 1981, Bahrain.



Figure 3-10-1 – Brine corrosion at a flange connection.



Figure 3-10-2 – Close-up of brine corrosion on flange in Figure 3-10-1.

3.11 Brittle Fracture

3.11.1 Description of Damage

Brittle fracture is the sudden rapid fracture under stress (residual or applied) where the material exhibits little or no evidence of ductility or plastic deformation. Although rare in refining operations, in-service brittle fracture of a pressure vessel or other pressurized equipment can have serious consequences.

3.11.2 Affected Materials

Carbon steels and low-alloy steels are of prime concern, particularly older steels. 400 series SS are also susceptible even if not embrittled. In addition, materials susceptible to an embrittling mechanism such as sigma phase embrittlement (3.56), 885 °F (475 °C) embrittlement (3.1), temper embrittlement (3.63), strain-aging embrittlement (3.60), or titanium hydriding (3.66) pose a risk for brittle fracture if they are sufficiently embrittled.

3.11.3 Critical Factors

- a) Brittle fracture can occur in a potentially susceptible piece of equipment containing a flaw or other significant stress concentrator. Three primary factors are:
 1. the material's fracture toughness (resistance to crack-like flaws) as indicated in a Charpy impact test or other fracture mechanics test;
 2. the size, shape, and stress concentration effect of the flaw; and
 3. the amount of residual and applied stresses on the flaw.
- b) Susceptibility of a material to brittle fracture may be increased by the presence of embrittling phases.
- c) Steel cleanliness (level of S, P, and other impurity elements) and grain size have a significant influence on toughness and resistance to brittle fracture. In addition, higher-strength, micro-alloyed steels can experience secondary hardening in certain temperature ranges due to the precipitation of embrittling phases that reduce the fracture toughness of the steel. Micro-alloying elements like V, Cb (Nb), B, and Ti in certain ranges as well as S, P, and Mn above their residual limits can cause low toughness.
- d) The heat treatment condition of the material can affect its fracture toughness.
- e) Thicker material sections have an inherently lower resistance to brittle fracture due to the nature of the stress state within a thick section of metal. Thick sections are under higher constraint (i.e. they are constrained from deforming), which increases triaxial stresses at the crack tip and promotes brittle, rather than ductile, fracture.
- f) In most cases, in materials that exhibit a ductile-to-brittle transition, brittle fracture occurs only at temperatures below the Charpy impact transition temperature (also called the ductile-to-brittle transition temperature), the temperature at and below which the toughness of the material drops off sharply.

3.11.4 Affected Units or Equipment

- a) Equipment manufactured to the ASME *Boiler and Pressure Vessel Code (BPVC)* Section VIII, Division 1, prior to the December 1987 Addenda, had no Code-required restrictions on notch toughness for vessels operating at cold temperatures. However, this does not mean that all vessels fabricated prior to this date will be subject to brittle fracture. Many designers, purchasers, and users specified supplemental impact tests on equipment that was intended to be in cold service.
 1. Equipment made to the same code after this date were subject to the requirements of UCS 66 (impact exemption curves), which address impact toughness requirements at low temperatures.
- b) Most processes run at elevated temperature, so the main concern is for brittle fracture during start-up, shutdown, or hydrotest/tightness testing. Thick wall equipment in particular in any unit should be evaluated.

- c) Brittle fracture resulting from an autorefrigeration event should be considered in units processing light hydrocarbons such as methane (CH₄), ethane/ethylene, propane/propylene, or butane. This includes alkylation units, olefin units, and polymer plants (polyethylene and polypropylene). Storage bullets and spheres for light hydrocarbons may also be susceptible.
- d) Brittle fracture can occur during ambient temperature hydrotesting due to high stresses and low toughness at the testing temperature.

3.11.5 Appearance or Morphology of Damage

- a) Cracks will typically be straight, non-branching, and largely devoid of any associated plastic deformation, although fine shear lips may be found along the free edge of the fracture, or localized necking around the crack may occur. (Figure 3-11-1 to Figure 3-11-5)
- b) The fracture surface, if undamaged after the initial fracture, will exhibit visible “chevron markings” that point back to the crack origin point. These markings can be helpful in locating the initiating cause of the brittle fracture. (Figure 3-11-6)
- c) Microscopically, the fracture surface will be composed largely of cleavage, with limited intergranular cracking and very little microvoid coalescence.

3.11.6 Prevention/Mitigation

- a) For most new equipment, brittle fracture is prevented by using materials compliant with UCS 66 in Section VIII of the ASME BPVC. In some cases, equipment will need to be specifically designed for low-temperature operation including upset and autorefrigeration events or will have additional requirements to account for a large wall thickness. Materials with controlled chemical composition, special heat treatment, and/or impact test verification may be required.
 - 1. Using fully killed, fine grain steel with austenite grain size finer than 6 (McQuaid Ehn Method) will achieve the desired toughness in many situations.
- b) For existing equipment, the combination of stress, material toughness, and existing or potential flaw size govern the probability of a brittle fracture event. In cases where there is a concern for the possibility of a brittle fracture occurring, an engineering evaluation can be performed in accordance with API 579-1/ASME FFS-1, Section 3, Level 1 or 2.
- c) Preventing and minimizing the possibility of a brittle fracture in existing equipment rely upon controlling the operating conditions (pressure, temperature), minimizing pressure at ambient temperatures during start-up and shutdown, not hydrotesting at too low a temperature, and periodic inspection at high-stress locations, as applicable to the specific situation. A pressure vessel can also be re-rated to a lower maximum allowable working pressure (MAWP) and resulting new, higher minimum design metal temperature (MDMT), per the requirements of the *National Board Inspection Code*, ASME BPVC Section VIII, Division 1, or other jurisdictional requirements or codes.
- d) Where brittle fracture is deemed a concern, some reduction in the likelihood of a brittle fracture may be achieved by following API 579-1/ASME FFS-1.
- e) In some cases, selecting or changing to a material with good low-temperature toughness, e.g. an appropriate low-temperature ASTM/ASME grade of steel (often containing a few percent of nickel) or an austenitic (300 series) stainless steel, will be necessary to achieve the desired low-temperature fracture toughness.

3.11.7 Inspection and Monitoring

- a) Routine inspection is not normally used to detect or mitigate brittle fracture, but awareness of susceptible equipment can help prevent future damage.

- b) Susceptible vessels can be inspected for pre-existing crack-like fabrication flaws, as well as for cracking from relevant in-service cracking mechanisms using magnetic particle testing (MT), PT, and/or UT, as applicable.

3.11.8 Related Mechanisms

Temper embrittlement (3.63), strain age embrittlement (3.60), 885 °F (475 °C) embrittlement (3.1), titanium hydriding (3.66), and sigma embrittlement (3.56).

3.11.9 References

1. API 579-1/ASME FFS-1, *Fitness-For-Service*, American Petroleum Institute, Washington, DC.
2. J.A. Smith and S.T. Rolfe, *Part 1: Constraint Effects on Fracture Behavior: The Effect of Crack Depth (a) and Crack-depth to Width Ratio (a/W) on the Fracture Toughness of A533-B Steel*, WRC Bulletin 418, Welding Research Council, Shaker Heights, OH.
3. British Standard 7910, *Guide to Methods for Assessing the Acceptability of Flaws in Metallic Structures*, British Standards Institution, London, UK.
4. ASME Boiler and Pressure Vessel Code (BPVC), *Section III: Rules for Constructions of Nuclear Facility Components; Division 1*, American Society of Mechanical Engineers, New York, NY.



Figure 3-11-1—20-in. carbon steel pipeline that failed during hydrotest at gouges on the OD.



Figure 3-11-2—Close-up of Figure 3-11-1 showing the gouges and the fracture origin (arrow) in one of the gouges.



Figure 3-11-3—Brittle fracture of a 2.2-in. wall C-0.5Mo exchanger channel during hydrotest.



Figure 3-11-4—Brittle fracture of vessel shell during hydrotest.

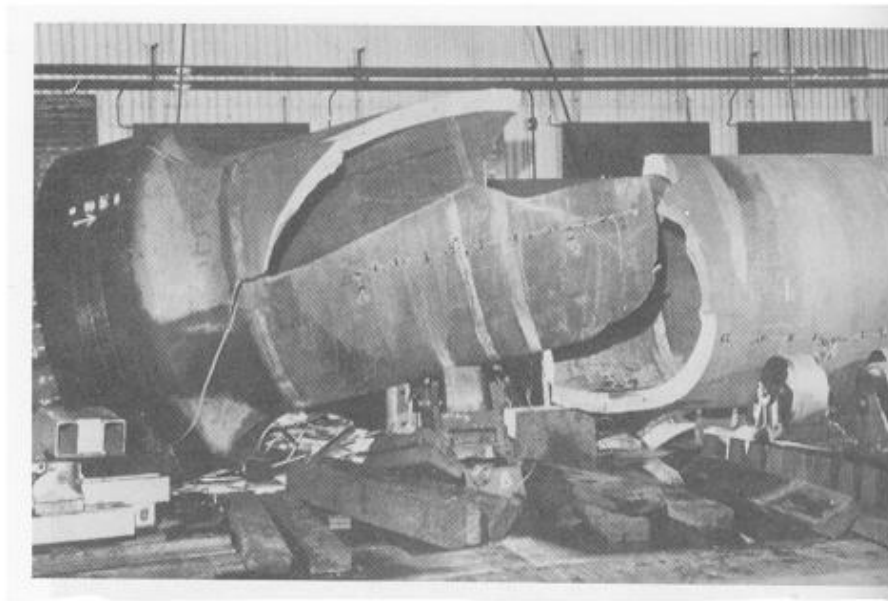


Figure 3-11-5—Classic example of brittle fracture that occurred during hydrotest.



Figure 3-11-6—Close-up view of the fracture surface from a vessel made of A516-70N plate showing the chevron pattern that points back toward the origin of the crack.

3.12 Carbonate Stress Corrosion Cracking

3.12.1 Description of Damage

- a) Carbonate SCC, more correctly *alkaline* carbonate SCC (ACSCC), but often referred to as carbonate cracking, occurs in process units containing a free water phase with carbonate ions and where some amount of H₂S is invariably also present.
- b) A related type of damage occurs in other environments, causing external cracking of buried pipelines and cracking of piping and equipment handling aqueous carbonate solutions (e.g. potassium carbonate) used for CO₂ removal in hydrogen manufacturing (steam-methane reforming) units. However, these situations are outside the scope of this discussion.

3.12.2 Affected Materials

Carbon steel and low-alloy steels with welds or cold-worked areas.

3.12.3 Critical Factors

- a) The weld or cold-worked area must have tensile residual stress and must be in contact with a liquid water phase. The water chemistry is a critical factor affecting the likelihood of carbonate SCC. Cracking is thought to occur when protective surface films (e.g. iron carbonate, iron sulfide, or iron oxides) break down and cannot re-form.
- b) Carbonate cracking can occur at relatively low levels of residual stress, but it usually occurs at welds or cold-worked areas that have not been stress relieved.
- c) Crack growth can be sporadic, but rapid, depending on subtle changes in the process.
- d) Additional details of water chemistry affecting susceptibility in FCC units are outlined below. More detailed information can be found in Reference 5.
 - 1. pH—The pH of the SW is a critical factor. Based on industry experience, ACSCC does not occur below pH 7. Susceptibility exists in the pH 7.5 to 11 range; however, most failures have occurred in the pH range of 8 to 10. Likelihood increases with increasing pH.
 - 2. H₂S—While cracking occurs alkaline (containing NH₃) water, H₂S is also present in these systems. Destruction of a protective iron sulfide film is thought to be the precursor to carbonate cracking in FCC SWs; however, no threshold level of H₂S affecting carbonate SCC has been established.
 - 3. Ammonia—NH₃ in the SW, which increases the pH, is usually higher in streams where ACSCC has been observed than in cases with no ACSCC. Streams with higher NH₃ and lower H₂S will have a higher pH, which increases the percentage of total carbonate present as carbonate ion and thereby increases the likelihood of ACSCC.
 - 4. Carbonate Ion Concentration—Cracking occurs above a certain threshold concentration of carbonate ions. It has been suggested that levels above 100 ppmw can cause ACSCC, depending on the pH of the system. However, specific thresholds are difficult to define, largely because of the difficulty of sampling and analyzing SW streams for carbonate ions along with the lack of available data.
 - 5. Sulfide-to-Carbonate Ratio—Low ratios of S²⁻ to CO₃²⁻ weaken the protective sulfide scale on steel and increase the likelihood of cracking.
 - 6. Cyanides—Cracking can occur with or without the presence of cyanides.
 - 7. Polysulfides—There is no evidence to suggest that ammonium polysulfide injection increases or decreases the potential for ACSCC.

- e) FCC unit feed quality and unit operation appear to have an effect on cracking susceptibility.
1. Feed Nitrogen—The total nitrogen in FCC unit feed is usually higher in cases where ACSCC has been observed than in cases with no ACSCC. Nitrogen compounds tend to increase SW pH.
 2. Feed Sulfur—In general, cracking is associated with low-sulfur FCC unit feeds as opposed to high-sulfur feeds. Susceptibility to cracking appears to be much more likely with hydrotreated feed.
 3. S-to-N Ratio—Most cases of ACSCC have been associated with a lowering of the S/N ratio in the FCC unit feed to less than 5.
 4. Full Burn vs Partial Burn—Full burn increases the regenerator O₂ level, which increases the amount of CO₂ produced and carried back into the reactor. This can directionally increase the tendency for cracking but may be offset by pH depression from increased CO/CO₂ content.
 5. Distillate vs Naphtha Optimization—Increasing distillate production from the FCC tends to favor reduced riser temperatures and increased catalyst circulation rates, both of which can increase the flue gas slip back to the reactor and thus the carbonate ion content of the SW streams.

3.12.4 Affected Units or Equipment

- a) Carbonate cracking has been most prevalent in FCC unit main fractionator overhead condensing and reflux systems, downstream wet gas compression systems, and the SW systems emanating from these areas. Both piping and vessels are affected. See [Figure 3-12-1](#) and [Figure 3-12-2](#) for typical locations where cracking has occurred.
- b) Carbonate SCC has also been observed in the regenerator (cold wall) shell.
- c) Carbonate cracking has been observed in pumparound-type SWS units, in the top pumparound and in the ammonia acid gas knockout sections. It has also occurred in highly cold worked pumparound cooler tube u-bends on the OD (process side).
- d) Carbonate cracking has also occurred in the floor of a tank storing SW from an FCC unit and in a mercaptan oxidation prewash vessel.
- e) Field welds may have higher potential for cracking if high restraint is introduced when making the joint fit-up.

3.12.5 Appearance or Morphology of Damage

- a) Carbonate cracks are surface breaking and typically propagate parallel to the weld in the HAZ or adjacent base metal within 2 in. (50 mm) of the weld. At least two cases have occurred more than 3 in. (80 mm) away in highly cold worked fittings including an elbow and reducer.
- b) Cracking can also occur in the weld deposit.
- c) The pattern of cracking observed on the steel surface is sometimes described as a spider web of small cracks, which often initiate at or interconnect with weld-related flaws that serve as stress risers.
- d) Carbonate cracks are usually found further away from the toe of the weld than cracks resulting from SSC or SOHIC [see (3.67)] and may show up as multiple cracks parallel to a weld. ([Figure 3-12-3](#) and [Figure 3-12-4](#)) The appearance of multiple parallel cracks may be related to the low stress required to continue propagating cracks in a loosely adherent scale.
- e) Carbonate cracks are predominantly intergranular and typically appear as a network of very fine, oxide-filled cracks similar in appearance to caustic SCC and amine SCC. (See [Figure 3-12-5](#) to [Figure 3-12-12](#).)

3.12.6 Prevention/Mitigation

- a) Application of a post-fabrication stress-relieving heat treatment of 1200 °F to 1225 °F (650 °C to 665 °C) in accordance with WRC 452 and WRC 552 (References 8 and 9) is a method of preventing ACSCC. Heat treatment requirements apply to construction and repair welds as well as internal and external attachment welds.
 - 1. PWHT of highly restrained welds made in the field may still have substantial residual stress remaining after PWHT. (Reference 8)
- b) Cracking can be eliminated through the use of effective barrier coatings, solid or clad 300 series SS, Alloy 400, or other corrosion-resistant alloys in lieu of carbon steel.

3.12.7 Inspection and Monitoring

- a) Monitoring the pH of SWs is the most practical and cost-effective method to locate areas where there is a potential for carbonate cracking to occur. Periodic monitoring of pH and CO_3^{2-} levels should be undertaken to determine the potential for cracking, with concern raised at pH 8 or higher. Sampling and analysis procedures should be verified before their use on highly buffered SW streams.
- b) Although cracks may be seen visually, crack detection is best performed with WFMT or ACFM techniques. Surface preparation by grit blasting, high-pressure water blasting, flapper wheel abrasive grinding, or other methods is usually required for WFMT.
- c) PT usually cannot find tight or scale-filled cracks and is not recommended.
- d) Angle beam UT (SWUT or PAUT) and ECT are effective techniques for crack detection and sizing.
- e) Electrical resistance type instruments that measure crack depth are not effective because the cracks typically contain magnetic iron oxide.
- f) This cracking is not susceptible to extension by grinding. Grinding out the cracks is a viable method of crack depth determination.
- g) AET can be used for locating cracks and monitoring crack growth.

3.12.8 Related Mechanisms

Amine cracking (3.3) and caustic SCC (3.15).

3.12.9 References

1. J.H. Kmetz and D.J. Truax, "Carbonate Stress Corrosion Cracking of Carbon Steel in Refinery FCC Main Fractionator Overhead Systems," Paper No. 206, *Corrosion/90*, NACE International, Houston, TX.
2. H.U. Schutt, "Intergranular Wet Hydrogen Sulfide Cracking," Paper No. 454, *Corrosion/92*, NACE International, Houston, TX.
3. E. Mirabel et al., "Carbonate-type Cracking in an FCC Wet Gas Compressor Station," *Materials Performance*, July 1991, pp. 41–45.
4. NACE Standard RP0296, *Guidelines for Detection, Repair, and Mitigation of Cracking of Existing Petroleum Refinery Pressure Vessels in Wet H₂S Environments*, NACE International, Houston, TX.
5. NACE Publication 34108, *Review and Survey of Alkaline Carbonate Stress Corrosion Cracking in Refinery Sour Waters*, NACE International, Houston, TX, 2008.

6. M. Rivera et al., "Carbonate Cracking Risk Assessment for an FCCU Gas Plant," Paper No. 04639, *Corrosion/2004*, NACE International, Houston, TX.
7. D. Milton et al., "FCCU Light Ends Plant Carbonate Stress Corrosion Cracking Experience," Paper No. 07564, *Corrosion/2007*, NACE International, Houston, TX.
8. WRC Bulletin 452, *Recommended Practices for Local Heating of Welds in Pressure Vessels*, Welding Research Council, Shaker Heights, OH, June 2000.
9. WRC Bulletin 552, *Calculation of Weld Residual Stresses and the Effects of Local Post-weld Heat Treatment*, Welding Research Council, Shaker Heights, OH, May 2016.
10. J. Nelson et al., "Carbonate Cracking Experiences in Unusual Locations," Paper No. 9596, *Corrosion/2017*, NACE International, Houston, TX.

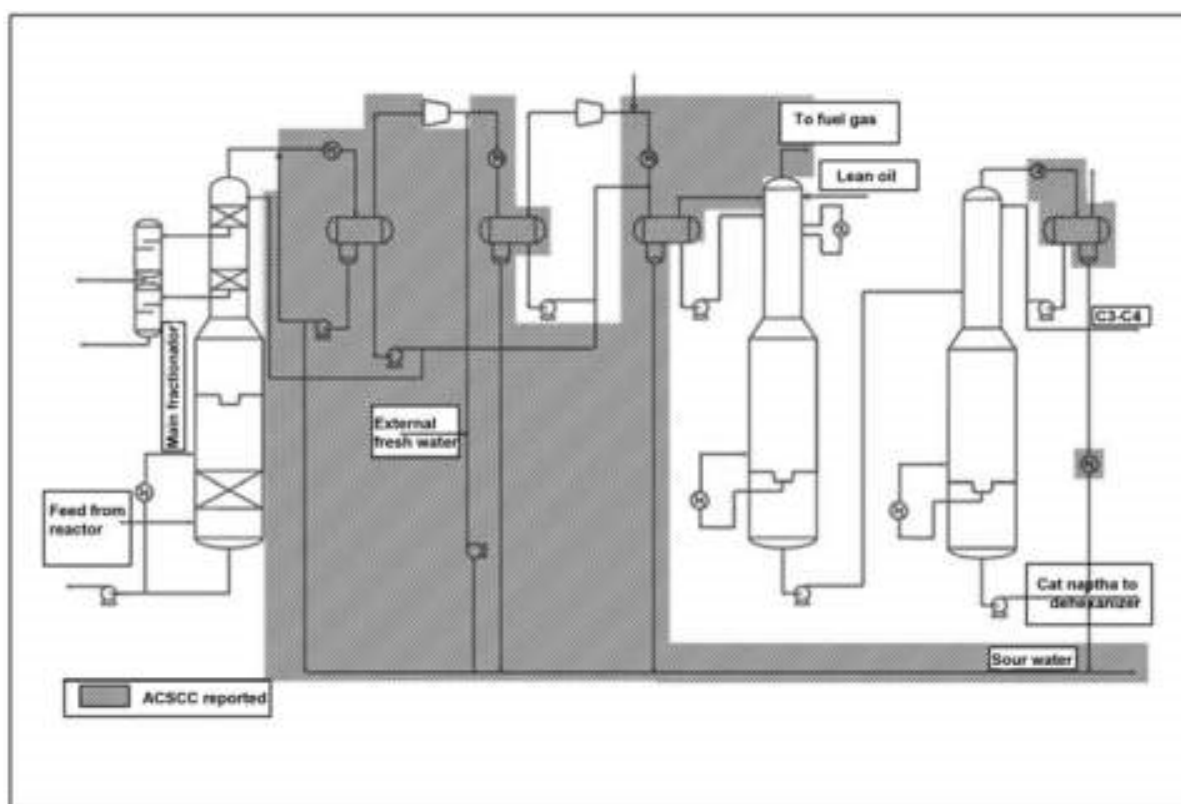


Figure 3-12-1—Simplified PFD of an FCC unit gas plant showing where ACSCC has been reported. (Reference 5)

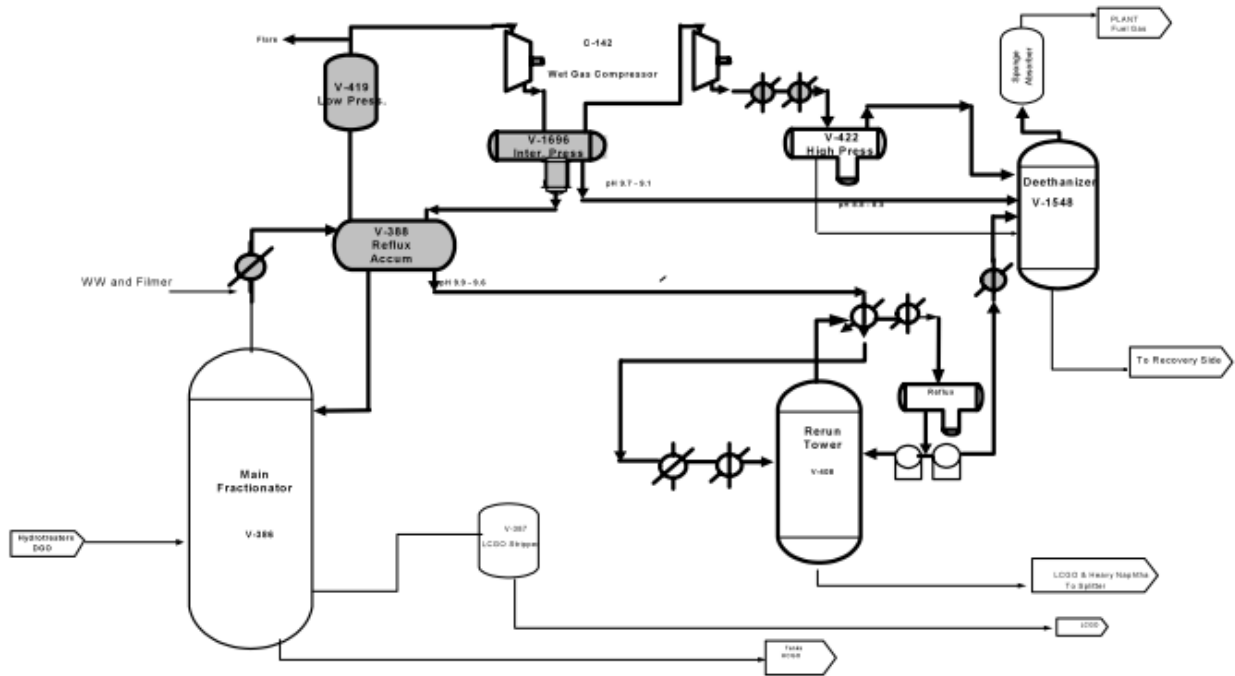


Figure 3-12-2—In a span of 7 months, a refinery experienced 23 leaks in piping in the fractionator overhead and the wet gas compressor sections. Follow-up with SWUT located 73 more indications. (Reference 6)



Figure 3-12-3—Carbonate cracking in an overhead interstage knockout drum vapor outlet nozzle.

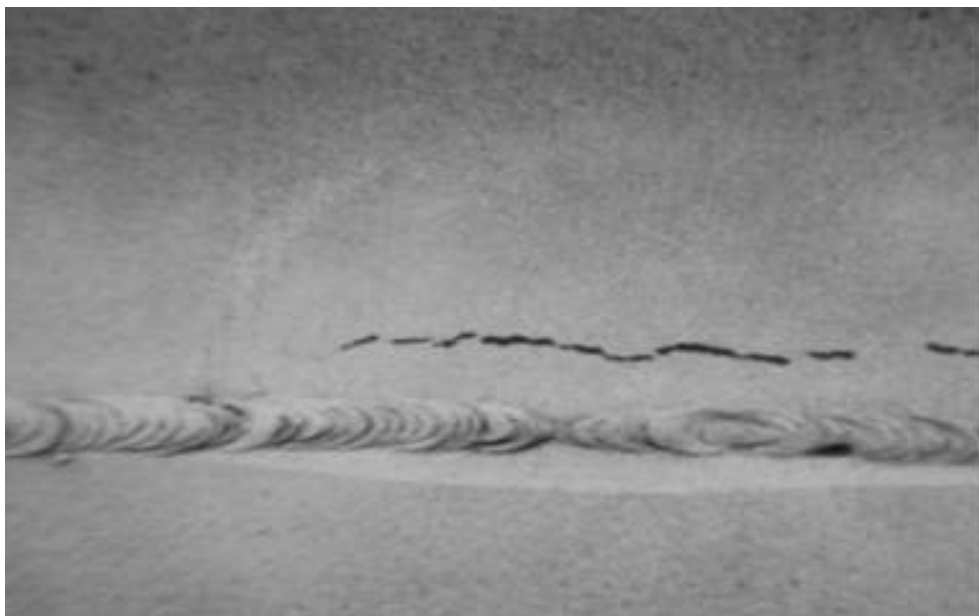


Figure 3-12-4—Carbonate cracking adjacent to a weld. (Reference 6)

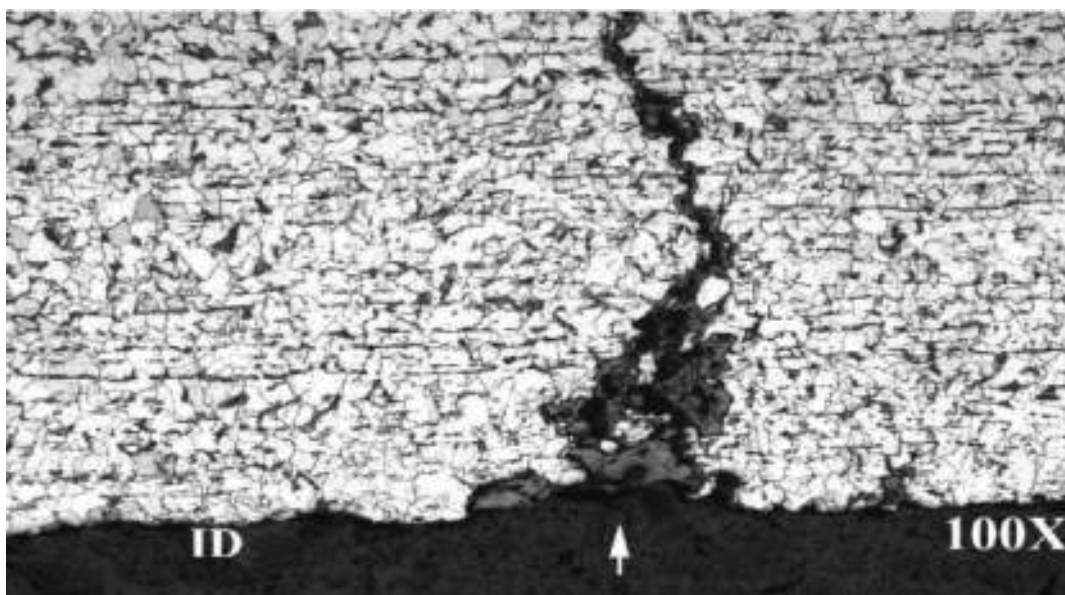


Figure 3-12-5—Metallographic sample showing intergranular carbonate cracking that developed after 6 months of service. (Reference 6)



Figure 3-12-6—Most cracks originate in base metal, but this weldment contained a crack that originated at the root and propagated through the weld metal. Other cracks appear to have initiated in the HAZ. (Reference 7)

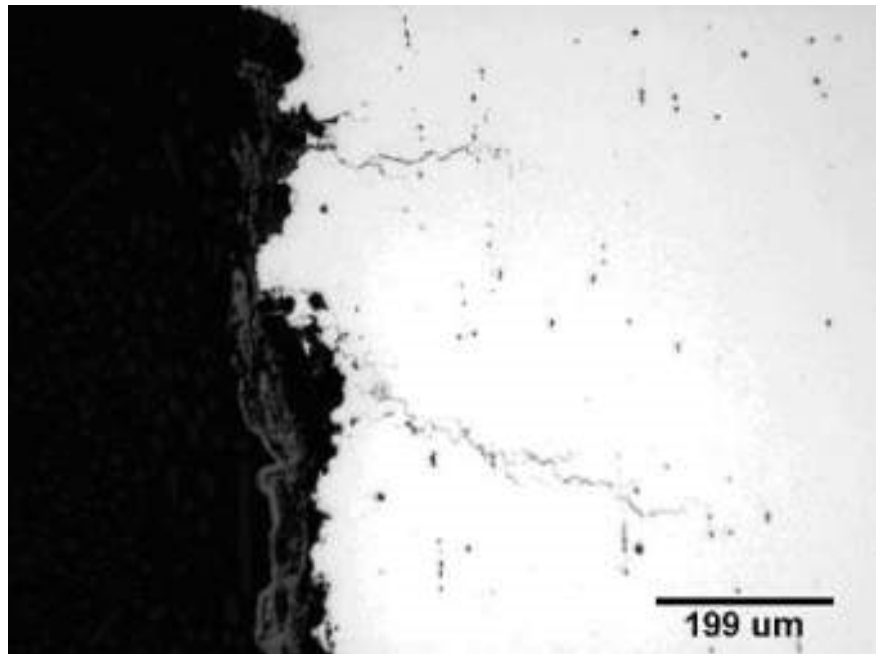


Figure 3-12-7—Photomicrograph of carbonate cracking in the base metal. Cracks initiated from the ID surface (left side). Unetched.

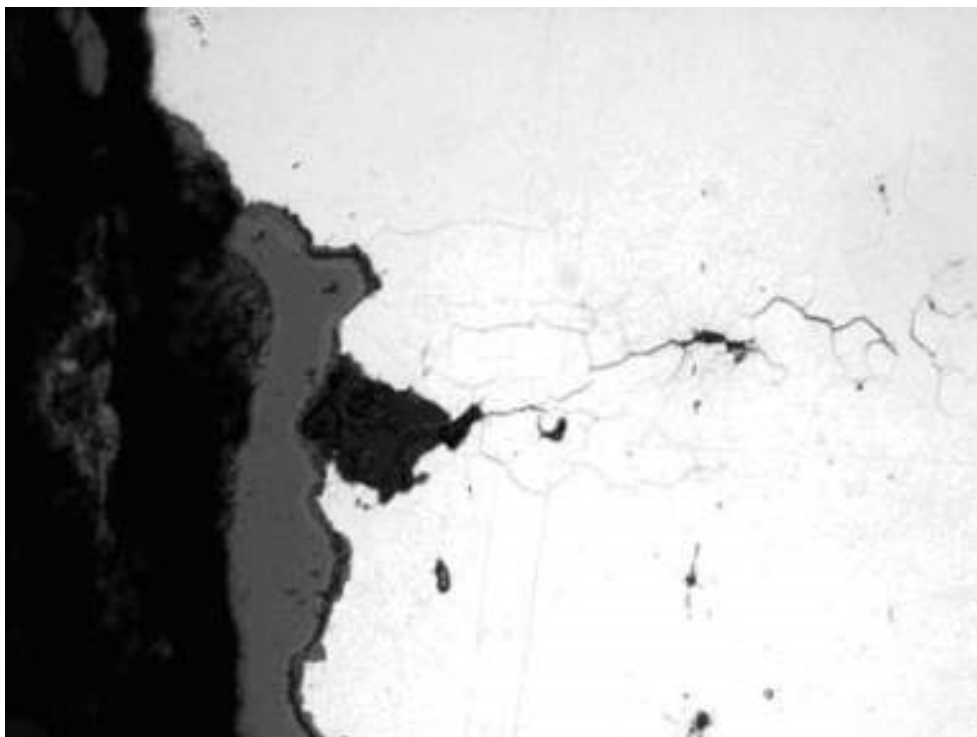


Figure 3-12-8—Photomicrograph of carbonate cracking in the base metal, initiating at a corrosion pit on the ID surface. Unetched.

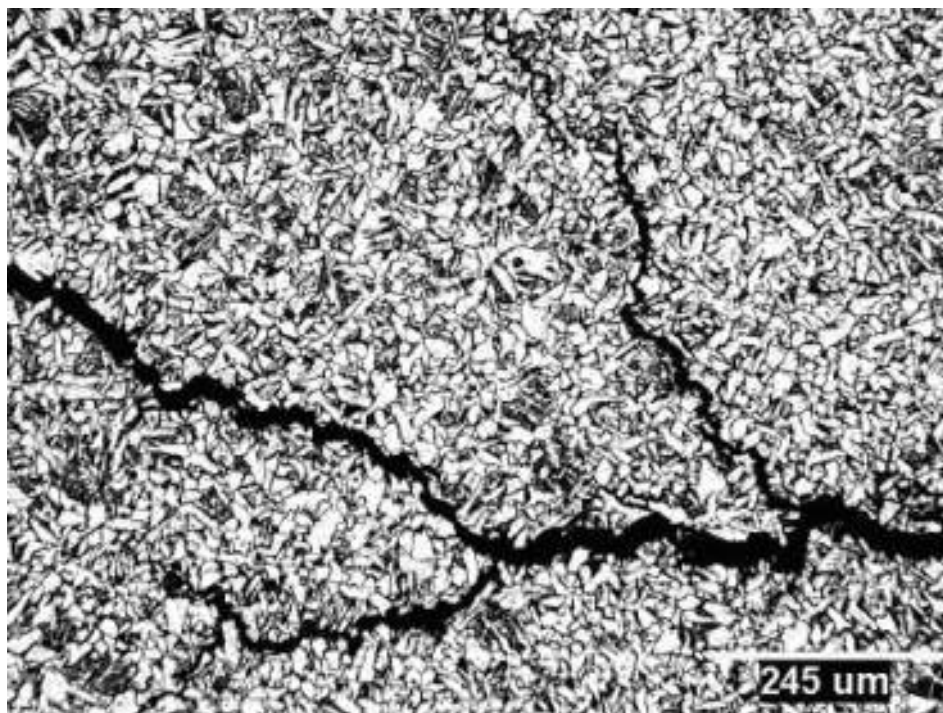


Figure 3-12-9—Photomicrograph of carbonate cracking in the base metal, showing the branched nature of the cracking. Etched.

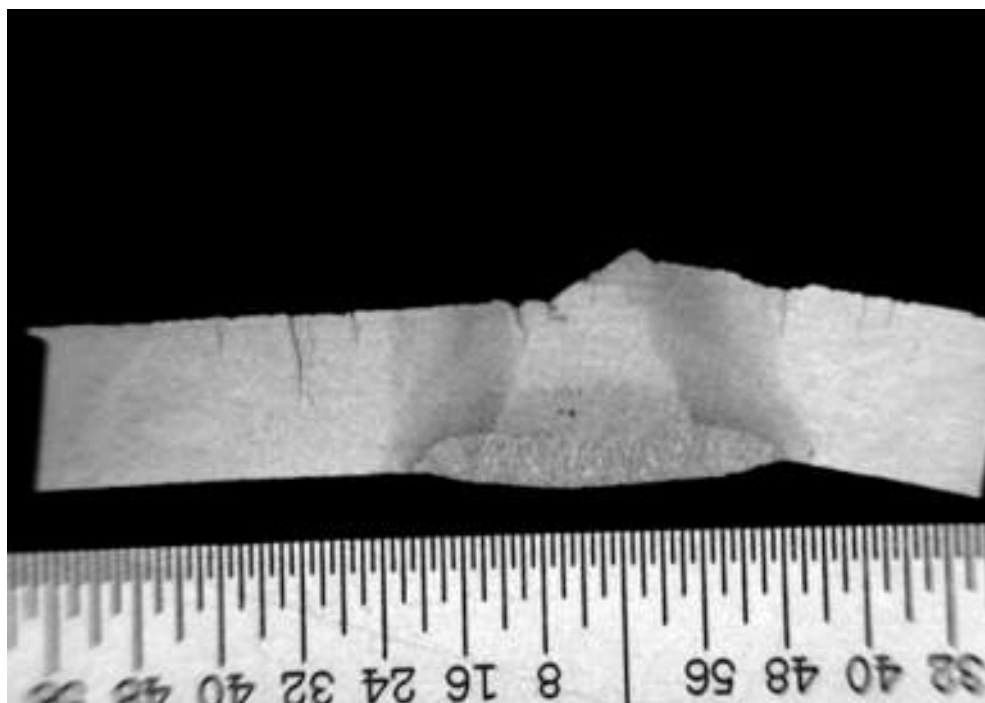


Figure 3-12-10—A weld from a 4-in. (100 mm) ASTM A53 reflux line on the main fractionator that leaked after 52 years of service.

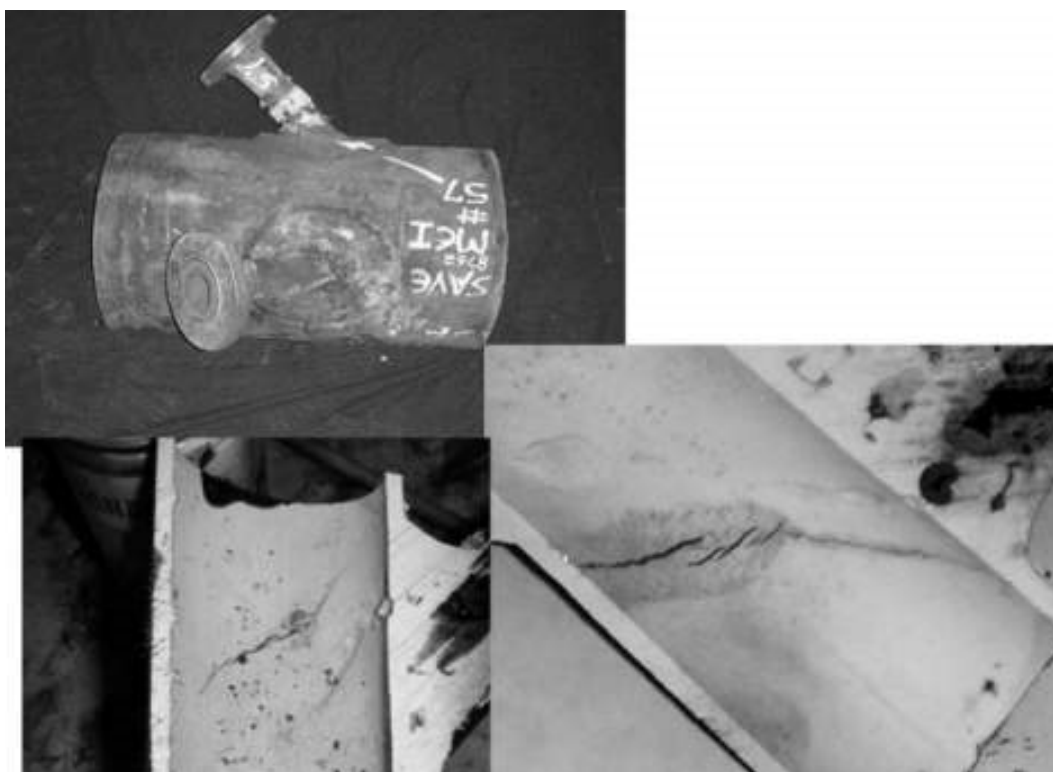


Figure 3-12-11—An 18-in. (460-mm) diameter API 5L Grade B pipe section with two 1-in. (25-mm) water wash injection nozzles from the inlet to the 2nd stage compressor. Note the cracks on the IDs of the two injection nozzles after blast cleaning. The line leaked after 21 years of service.



Figure 3-12-12—A 3-in. x 4-in. (75-mm x 100-mm) diameter tee in a hydrocarbon line off a water knockout pot in the FCC light ends recovery section. Cracking developed after 6 months of service.

3.13 Carburization

3.13.1 Description of Damage

Carbon is absorbed into a material at elevated temperature while in contact with a carbonaceous material or carburizing environment. Carburized steel is brittle and may spall or crack. Carburization can reduce (or eliminate) the remaining sound metal wall thickness and may also reduce the corrosion resistance of stainless steel.

3.13.2 Affected Materials

Carbon steel and low-alloy steels, 300 series SS and 400 series SS, cast stainless steels, nickel base alloys with significant iron content (e.g. Alloys 600 and 800), and HK/HP alloys.

3.13.3 Critical Factors

- a) Three conditions must be satisfied:
 - 1. exposure to a carburizing environment or carbonaceous material;
 - 2. temperature high enough to allow diffusion of carbon into the metal [typically above 1100 °F (595 °C)];
 - 3. susceptible material.
- b) Conditions favoring carburization include a high gas phase carbon activity (hydrocarbons, coke, gases rich in CO, CO₂, CH₄, ethane) and low oxygen potential (minimal O₂ or steam).
- c) Initially, carbon diffuses into the component at a high rate and then tapers off as the depth of carburization increases.
- d) In carbon steels and low-alloy steels, carbon reacts to form a hard, brittle structure at the surface that may crack or spall upon cooling.
- e) 300 series SS are more resistant than carbon steel and low-alloy steels due to their higher chromium and nickel content.
- f) Carburization of 300 series SS can result in a reduction of chromium levels available to provide corrosion protection. This has caused accelerated sulfidation of 300 series SS in coker furnaces.
- g) Carburization can result in the loss of high-temperature creep ductility, loss of ambient temperature mechanical properties (specifically toughness/ductility), loss of weldability, and reduced corrosion resistance.

3.13.4 Affected Units or Equipment

- a) Fired heater tubes are the most common type of equipment susceptible to carburization in the environments mentioned earlier.
- b) Coke deposits are a source of carbon that may promote carburization, particularly during steam/air decoke cycles where temperatures exceed the normal operating temperatures, accelerating the carburization.
- c) Carburization is sometimes found in heater tubes in catalytic reformers and coker units or other heaters where coke can form.
- d) Carburization is also encountered in ethylene pyrolysis and steam reformer furnaces.

3.13.5 Appearance or Morphology of Damage

- a) The depth of carburization can be confirmed by metallography. ([Figure 3-13-1](#) and [Figure 3-13-2](#))

- b) Carburization can be confirmed by substantial increases in hardness and loss in ductility.
- c) In a more advanced stage, there may be a volumetric increase in the affected component. In this situation, carbides that form can cause the surrounding metal to “crumble” due to the increase in volume. This has been termed “catastrophic carburization” and has resulted in significant metal loss over an extended period of time.
- d) Severe cases may also result in bulges, heavy scale, thin-line brittle cracking, and/or “thick-lip” tube failures. Cracking can also have a “crow’s feet” appearance.
- e) A change (increase) in the level of ferromagnetism can occur in some alloys.
- f) Carburization results in the formation of metal carbides depleting the surrounding matrix of the carbide-forming element.

3.13.6 Prevention/Mitigation

- a) Select alloys with adequate resistance to carburization. This typically includes alloys that form stable oxides on the surface. This benefit is commonly achieved using an alumina-forming coating commonly referred to as alonizing.
- b) Reduce the carbon activity of the process environment.
- c) Add low levels of a reactive sulfur compound to the process stream to prevent the absorption of carbon on the surface of the metal. Typically, sulfur levels less than 10 ppm are needed to prevent carburization.

3.13.7 Inspection and Monitoring

- a) VT is ineffective in detecting carburization. A-scan UT is ineffective at determining carburized thickness.
- b) Carburization can be determined accurately by destructive sampling, i.e. sampling for chemical and/or physical testing.
- c) Inspection for carburization in the initial stages of attack is difficult. If the process-side surfaces are accessible, hardness testing and field metallography (replication) can be used. Destructive sampling and electromagnetic based techniques (eddy current) have also been used.
 - 1. In situ metallography (replication) is rarely used alone for evaluation of carburization and is best used in combination with other NDE techniques.
 - 2. Hardness testing carries the same caution as hammer testing for heavily carburized tubes, as it may create a brittle fracture initiation site.
- d) Carburization causes the normally nonmagnetic wrought and cast heat-resistant alloys to become magnetic. The resulting magnetic permeability provides a methodology for monitoring the extent of carburization damage. Inspection techniques based on determining increased levels of ferromagnetism (magnetic permeability) are also useful for alloys that are paramagnetic when initially installed (austenitic alloys).
- e) Measurement devices range from simple hand-held magnets to advanced multi-frequency eddy current instruments. However, surface oxides may interfere with the results.
- f) Some instruments and field services can relate the degree of magnetism to the depth of carburization. Most of the instruments are proprietary, and the field services are limited.
- g) In the advanced stages of carburization where cracking has initiated, RT, UT, and some magnetic techniques, which can be combined for effectiveness, may be used.

- h) Specialized time of flight diffraction (TOFD) has been used to determine the case depth of carburization but requires trained technicians for application and interpretation.
- i) Cast austenitic stainless steel tubes and Cr-Mo ferritic alloy tubes in fired heater/boiler service should not be hammer tested when tubes are heavily carburized.

3.13.8 Related Mechanisms

Metal dusting (3.44).

3.13.9 References

1. *ASM Handbook—Corrosion*, Volume 13, ASM International, Materials Park, OH.
2. H.J. Grabke, *Carburization: A High Temperature Corrosion Phenomenon*, Part 1: State-of-the-Art Review; Part 2: Best Practices for Testing Alloys, MTI Publication No. 52.
3. API Recommended Practice 939-C, *Guidelines for Avoiding Sulfidation (Sulfidic) Corrosion Failures in Oil Refineries*, American Petroleum Institute, Washington, DC
4. API Recommended Practice 573, *Inspection of Fired Boilers and Heaters*, American Petroleum Institute, Washington, DC.

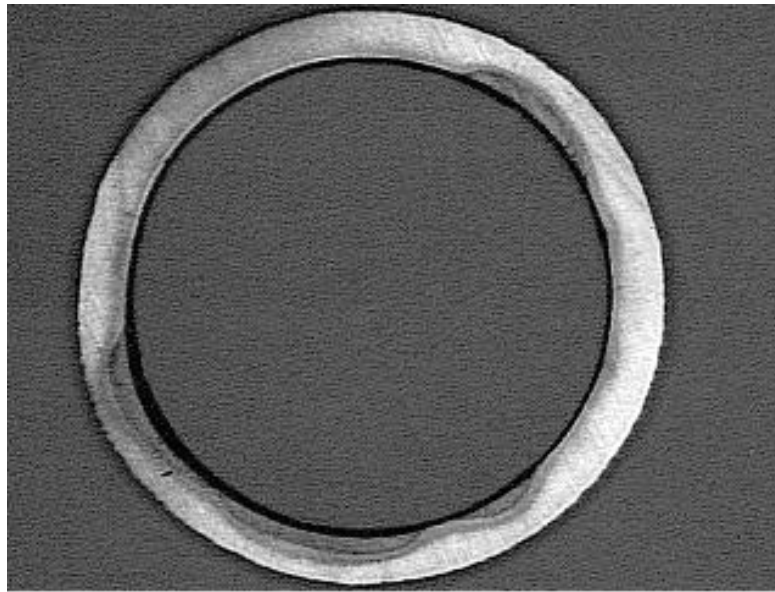


Figure 3-13-1—Carburization (dark areas) of an HP-modified tube from an ethylene furnace after 3 years at 1900 °F (1040 °C).

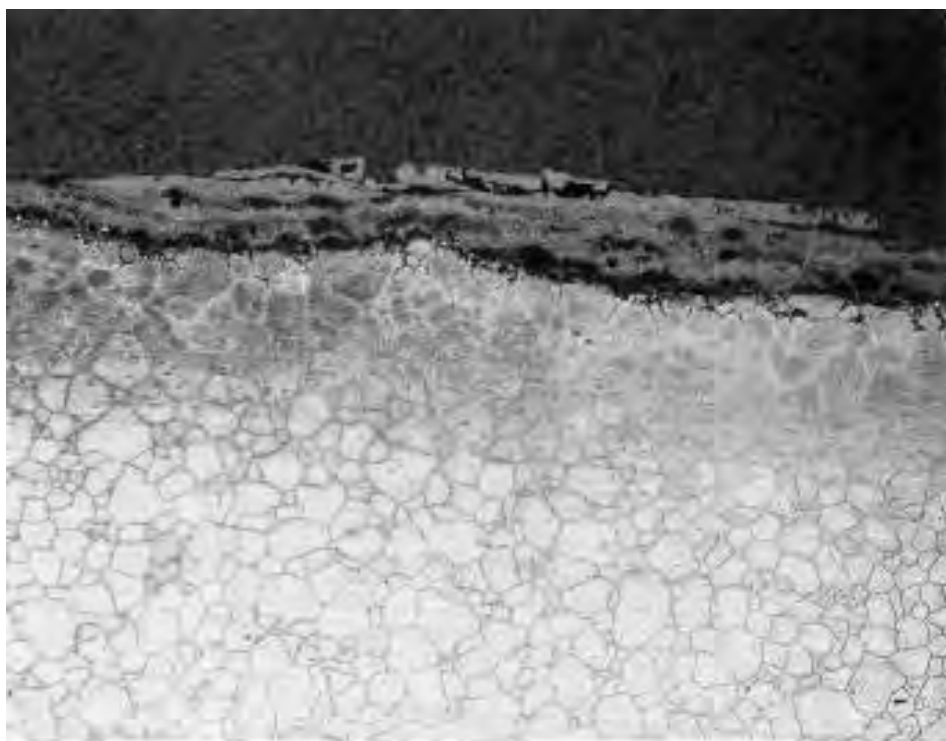


Figure 3-13-2—A photomicrograph of a cross section of a 304H cyclone from a fluid coker showing surface carburization after 24 years. Magnification 35X.

3.14 Caustic Corrosion

3.14.1 Description of Damage

Localized corrosion due to the concentration of caustic (alkaline) solutions such as NaOH and KOH, and/or corrosive salts from those solutions, that usually occurs under evaporative or high heat transfer conditions (commonly called caustic gouging). Also, corrosion resulting in general thinning can occur at elevated temperatures, depending on alkali or caustic solution strength.

3.14.2 Affected Materials

Primarily carbon steel, low-alloy steels, and 400 series SS. Carbon steel is the material most commonly used in situations where caustic corrosion is a concern. 300 series SS is generally resistant to caustic corrosion until passivity is damaged, which can occur in the approximate temperature range of 160 °F to 210 °F (70 °C to 100 °C), depending on the concentration. 300 series SS can also be susceptible to caustic SCC at these elevated temperatures. (See [3.15](#).)

3.14.3 Critical Factors

- a) Caustic (NaOH or KOH) must be present. The following are sources of caustic.
 - 1. Caustic is commonly added to treat BFW and may also enter inadvertently during regeneration of demineralizers.
 - 2. Caustic is sometimes added to process streams for acid neutralization or as a reactant to remove sulfur or chlorides.
 - 3. Alkaline solutions or salts may also enter process streams through leaks in condensers or other process equipment.
 - 4. Concentrated caustic is handled in the storage and feed equipment used for feeding caustic into BFW or process streams.
- b) In high-solution-strength caustic, temperatures above about 170 °F (75 °C), with the temperature limit depending on the caustic concentration, will cause general corrosion of carbon steel. (See [Figure 3-15-1](#) in [3.15](#) on caustic SCC.)
- c) For localized caustic gouging to occur, a concentrating mechanism must exist to build up the caustic strength or salt concentration.
 - 1. Caustic can become concentrated by departure from nucleate boiling (DNB), evaporation, and deposition of salts.
 - 2. Higher temperatures help produce a concentrating mechanism, thereby increasing the corrosivity of the solution while also generally increasing the corrosion rate.
- d) Some contaminants, such as chlorides and hypochlorites, are known to increase the corrosivity of caustic solutions.
- e) Heat tracing may sometimes contribute to this problem.

3.14.4 Affected Units or Equipment

- a) Localized caustic corrosion (caustic gouging) is most often associated with boilers and steam-generating equipment including heat exchangers. This also applies to steam-generating equipment in H₂ manufacturing units and steam generators within other process units.
- b) Similar concentrating effects of caustic can occur where caustic is added to crude unit feed.

1. Accelerated localized corrosion can occur in preheat exchangers, furnace tubes, and transfer lines, if the caustic is not effectively mixed in the oil stream.
- c) Units that use caustic for removing sulfur compounds from process streams can also be subject to caustic corrosion.
- d) Heat-traced tanks used for caustic storage and caustic feed equipment near the process injection location can suffer caustic corrosion if temperatures get too high.

3.14.5 Appearance or Morphology of Damage

- a) Caustic gouging is typically characterized by localized metal loss that may appear as grooves in a boiler tube or locally thinned areas under insulating deposits. (Figure 3-14-1 and Figure 3-14-2)
- b) Deposits may fill corroded depressions and mask damage below. Probing suspect areas with a sharp instrument may be required.
- c) Localized gouging may result along a waterline where corrosives concentrate. In vertical tubes, this may appear as a circumferential groove.
- d) In horizontal or sloped tubes, grooving may appear at the top of the tube or as longitudinal grooves on opposite sides of the tube.
- e) Corrosion of carbon steel in high-concentration caustic at elevated temperatures will be generalized but likely confined to the location of the high temperature, e.g. next to heat tracing.

3.14.6 Prevention/Mitigation

- a) In steam-generating equipment, caustic corrosion is best prevented through proper design. Damage can be minimized by reducing the amount of free caustic, by ensuring adequate water flooding and water flow, by ensuring proper burner management to minimize hot spots on heater tubes, and by minimizing the ingress of alkaline producing salts into condensers.
- b) In process equipment, caustic injection facilities should be designed to allow proper mixing and adequate dilution of caustic in order to avoid the concentration of caustic on hot metal surfaces.
- c) Carbon steel (and stainless steels) have serious corrosion problems in high-strength caustic solutions at elevated temperatures. Alloy 400 and some other nickel-based alloys exhibit much lower corrosion rates.

3.14.7 Inspection and Monitoring

- a) General Corrosion—UT using a straight beam or UT scanning or other similar techniques can measure general loss.
- b) Localized Corrosion—Manual UT, including UT scanning, or AUT can be used. Angle beam (SWUT or PAUT) or TOFD may be necessary to determine the extent of localized corrosion. RT has also been used within the limits of the technique.
- c) Permanently mounted thickness monitoring sensors can be used.
- d) Heat or steam tracing can cause localized corrosion at the point of contact due to locally high temperatures or improper installation. This is an area to focus on for inspection.
- e) Caustic injection sites should be examined and monitored as discussed in API 570 and API 574.
- f) When internal access is not available (e.g. steam equipment, tubing, small-diameter equipment, or equipment with ports), VT may be performed using a boroscope.

3.14.8 Related Mechanisms

Caustic SCC (3.15). Caustic gouging has also been referred to as ductile gouging.

3.14.9 References

1. *ASM Handbook—Failure Analysis and Prevention*, Volume 11, ASM International, Materials Park, OH.
2. R.D. Port and H.M. Herro, *The Nalco Guide to Boiler Failure Analysis*, McGraw-Hill, New York, NY, 1991, pp. 58–70.



Figure 3-14-1—ID deposits on carbon steel boiler tube with damage due to caustic corrosion.

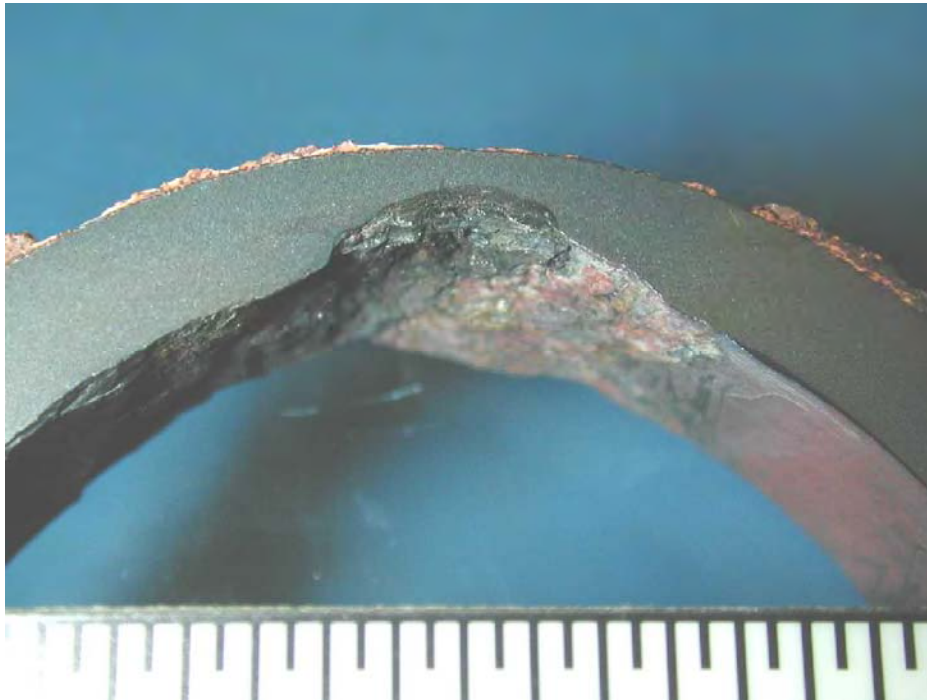


Figure 3-14-2—Cross section of tube in Figure 3-14-1 showing localized attack due to caustic corrosion.

3.15 Caustic Stress Corrosion Cracking

3.15.1 Description of Damage

Caustic SCC is characterized by surface-initiated cracks that occur in piping and equipment exposed to caustic (alkaline hydroxide solutions) at elevated temperature, primarily adjacent to non-PWHT'd welds. It is a form of ASCC. The temperature above which caustic SCC occurs depends on the concentration of the caustic solution.

3.15.2 Affected Materials

Carbon steel, low-alloy steels, and 300 series SS are susceptible. Duplex stainless steels are also susceptible but have shown improved resistance compared to the 300 series SS. Nickel-based alloys are more resistant.

3.15.3 Critical Factors

- a) Susceptibility to caustic SCC in caustic soda (NaOH) and caustic potash (KOH) solutions is a function of caustic strength, metal temperature, and stress level.
- b) Increasing caustic concentration and increasing temperature increase the likelihood and rate of cracking. Conditions likely to result in cracking have been established through plant experience and are presented in [Figure 3-15-1](#).
- c) Cracking can occur at low caustic levels if a concentrating mechanism is present. In such cases, caustic concentrations of 50 ppm to 100 ppm are sufficient to cause cracking.
- d) Residual stresses from welding (in non-stress-relieved welds) or from cold working (such as bending and forming) will cause cracking, and these high residual stresses are what typically lead to caustic SCC. ([Figure 3-15-2](#) to [Figure 3-15-8](#)) Applied stresses, e.g. from pressure or mechanical loading, can also cause caustic SCC, but this is uncommon since applied stresses are normally low relative to the yield point and are lower than residual stresses from welding or forming.
- e) Thermal stress relief (PWHT) is effective in preventing caustic SCC. ([Figure 3-15-1](#))
- f) Crack propagation rates increase dramatically with temperature, and cracks can grow through wall in a matter of hours during temperature excursions, especially in concentrated caustic or if conditions promote caustic concentration. Concentration can occur as the result of alternating wet and dry conditions, localized hot spots, or high-temperature steam out.
- g) Special care must be taken with steam tracing or heat tracing design as well as steam out of non-PWHT'd piping and equipment.
- h) Contaminants in the caustic solution, especially sulfides, regardless of concentration, will increase the likelihood of SCC in non-PWHT'd carbon steel, including in the lower temperature area (area "A") in [Figure 3-15-1](#).

3.15.4 Affected Units or Equipment

- a) Caustic SCC can occur in non-stress-relieved piping and equipment that handles caustic, including H₂S and mercaptan removal units, as well as equipment that uses caustic for neutralization in sulfuric acid alkylation units and HF alkylation units. Caustic is sometimes injected into the feed to the crude tower for chloride control.
- b) Failures have occurred in improperly heat-traced piping or equipment as well as heating coils and other heat transfer equipment.
- c) Caustic SCC can occur in equipment as the result of steam cleaning after being in caustic service.

- d) Traces of caustic can become concentrated in BFW and can result in caustic SCC of boiler tubes that alternate between wet and dry conditions due to overfiring. It can also occur in superheaters due to steam drum carryover.
- e) Cracking can occur in boilers at rolled tube joints due to caustic concentrating between the tube and tubesheet. (Figure 3-15-4)
- f) Caustic SCC can also occur as the result of unintended carryover of caustic into equipment not designed to handle hot caustic (e.g. not stress relieved), such as steam condensate piping or process equipment downstream of a caustic treating section of a process unit.

3.15.5 Appearance or Morphology of Damage

- a) Caustic SCC typically propagates parallel to the weld in adjacent base metal, i.e. in the zone of highest welding residual stress, but can also occur in the weld deposit or HAZ and can be transverse to the weld.
- b) The pattern of cracking observed on the steel surface is sometimes described as a spider web of small cracks that often initiate at or interconnect with weld-related flaws that serve as local stress risers.
- c) Cracks can be confirmed through metallographic examination. Cracks are typically branched and predominantly intergranular. Cracking that occurs in as-welded carbon steel typically appears as a network of very fine, oxide-filled cracks.
- d) Cracking in 300 series SS is most often transgranular but can be intergranular even in non-sensitized material. When transgranular, it can be difficult to distinguish from Cl^- SCC. Caustic SCC should exhibit a black magnetite layer on the crack surface, whereas Cl^- SCC should not produce that type of oxide scale.
- e) Similarly, caustic SCC of nickel-based alloys has been observed as either intergranular (Figure 3-15-9) or transgranular (Figure 3-15-10).

3.15.6 Prevention/Mitigation

- a) Cracking can be effectively prevented by means of a stress-relieving heat treatment (e.g. PWHT). A heat treatment at 1150 °F (620 °C) minimum with a minimum holding time of 1 hr is considered an effective stress relieving heat treatment for carbon steel. The same requirement applies to repair welds and to internal and external attachment welds.
 - 1. In contaminated caustic solutions, stress relief may be needed to prevent cracking of carbon steel even at low, otherwise “safe” temperatures (area “A” in Figure 3-15-1).
- b) 300 series SS offer little advantage in resistance to cracking over carbon steel.
- c) Nickel-based alloys are more resistant to cracking and may be required at higher temperatures and/or caustic concentrations. However, caustic SCC of these alloys has been observed at high temperatures that promote the formation of molten caustic in the absence of free water [604 °F (318 °C), at atmospheric pressure]. This damage has sometimes been referred to as molten caustic cracking.
- d) Steam out of non-PWHT'd carbon steel piping and equipment should be avoided. Where necessary, equipment should be water washed before steaming out, and only low-pressure steam should be used for short periods of time to minimize exposure.
- e) Proper design and operation of the injection system is required to ensure that caustic is properly dispersed before entering the high-temperature crude preheat system.
- f) Ensure all soda ash (sodium carbonate) solution that may have been used as a protective measure against polythionic acid stress corrosion cracking (PTA SCC) in 300 series SS equipment is drained prior to heating up as this soda ash can result in caustic SCC of 300 series SS as well as Alloy 800 and Alloy 825 as the water is boiled away.

3.15.7 Inspection and Monitoring

- a) WFMT, ACFM, and ECT can be effective techniques to detect these surface-breaking cracks. Proper surface preparation is necessary to ensure cracking is not masked by blending or smearing metal into the cracks. The method of surface preparation is dependent upon the specific technique.
- b) Angle beam ultrasonic techniques (SWUT and PAUT) can be effective to detect and size cracks. These ultrasonic techniques can be used to periodically monitor crack growth.
- c) PT or MT can be effective. PT may not be effective for finding tight cracks, because the cracks are oxide filled.
- d) RT may not be effective in detecting fine, tight cracks.
- e) AET can be used for locating cracks and monitoring crack growth.
- f) Severe cracking can at times be identified visually.

3.15.8 Related Mechanisms

Amine SCC (3.3) and carbonate SCC (3.12) are two other similar forms of ASCC. Caustic SCC has also been called caustic embrittlement, but this is a misnomer and an obsolete term. Caustic SCC is a SCC mechanism, not an embrittlement mechanism.

3.15.9 References

1. NACE 37519, *NACE Corrosion Data Survey—Metals Section*, Fifth Edition, NACE International, Houston, TX.
2. “Fitness-For-Service Evaluation Procedures for Operating Pressure Vessels, Tanks, and Piping in Refinery and Chemical Service,” Materials Properties Council, FS-26, Draft No. 5, Consultants Report, NY, 1995.
3. J.K. Nelson, “Materials of Construction for Alkalies and Hypochlorites,” *Process Industries Corrosion—The Theory and Practice*, NACE International, Houston, TX, 1986, pp. 297–310.
4. NACE SP0403, *Avoiding Caustic Stress Corrosion Cracking of Refinery Equipment and Piping*, NACE International, Houston, TX.
5. REFIN•COR, Corrosion Technology Week, 2011, NACE International, Houston, TX.
6. “Environmentally Assisted Cracking,” *ASM Handbook—Corrosion: Environments and Industries*, Volume 13C, ASM International, Materials Park, OH, 2007.

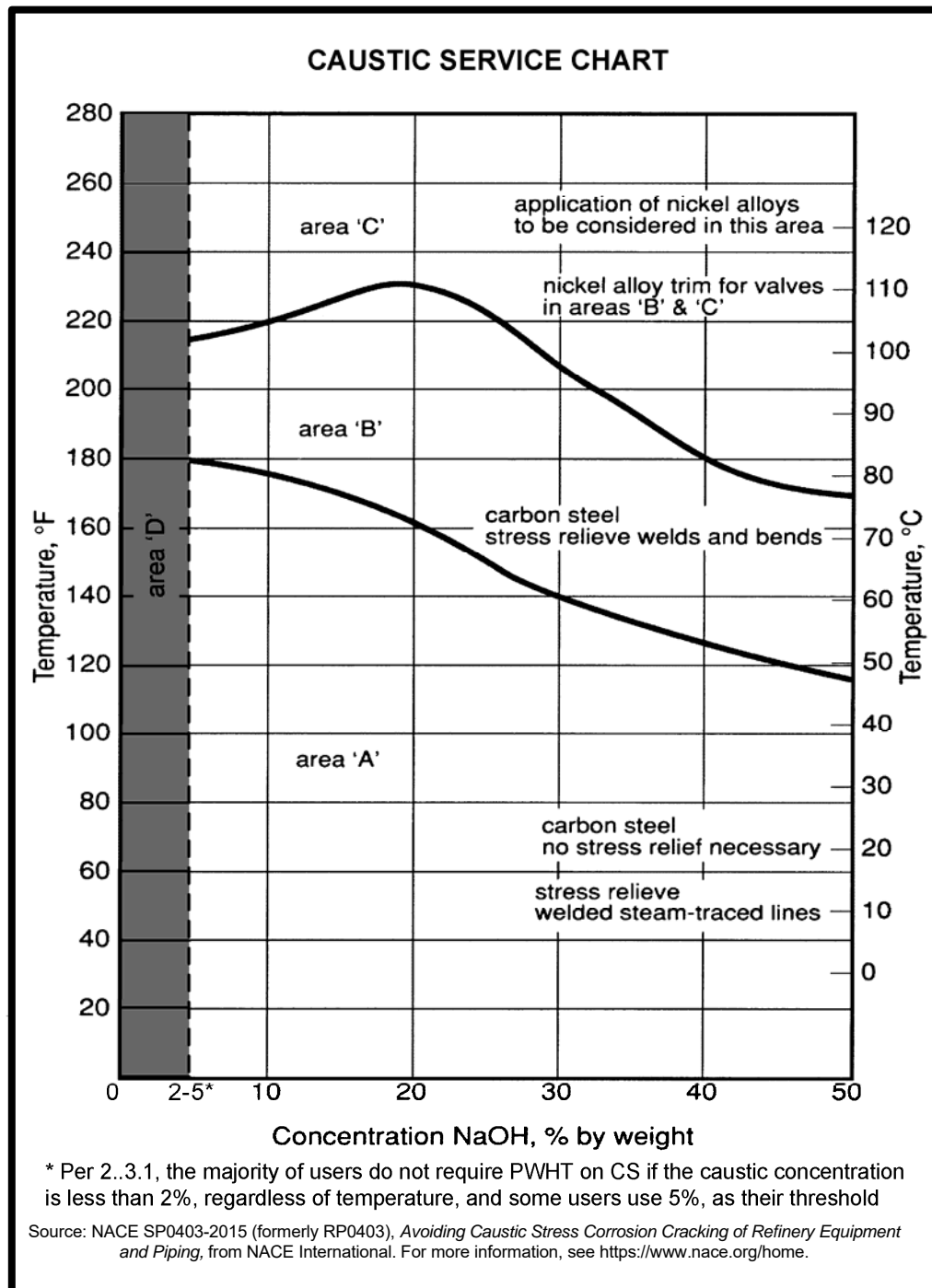


Figure 3-15-1—Recommended operating limits for carbon steel in caustic service. (Reference 4)

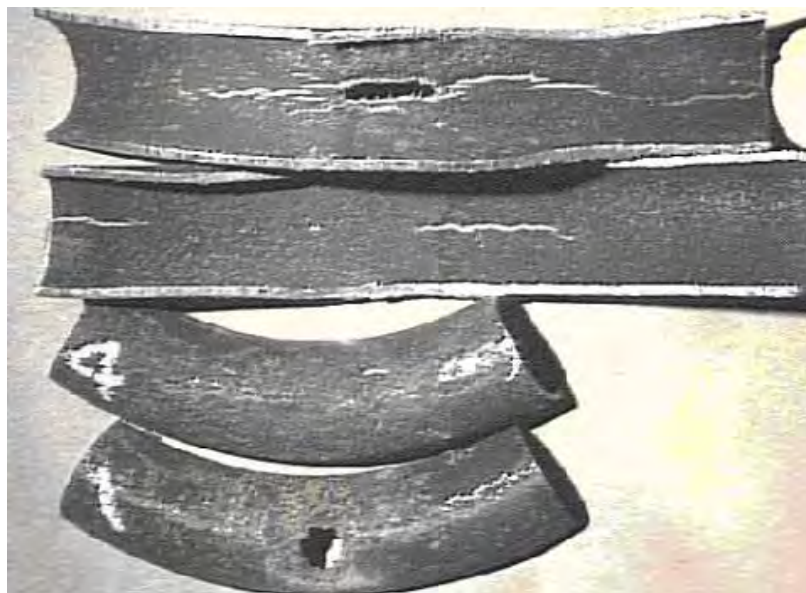


Figure 3-15-2—Cracking initiating on the inside surface of a non-stress-relieved carbon steel heat exchanger bend after 8 years in 15 % to 20 % caustic service at 140 °F to 240 °F (60 °C to 115 °C).



Figure 3-15-3—Photomicrograph of a crack in the tube shown in Figure 3-15-2.

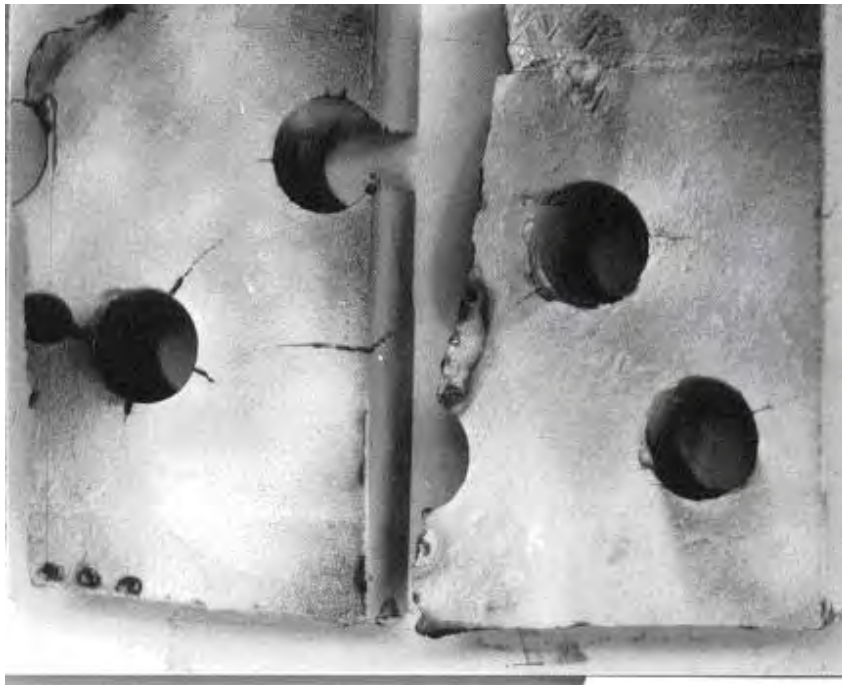


Figure 3-15-4—Cracking in a boiler tubesheet due to caustic concentrating between the tube and the tubesheet.

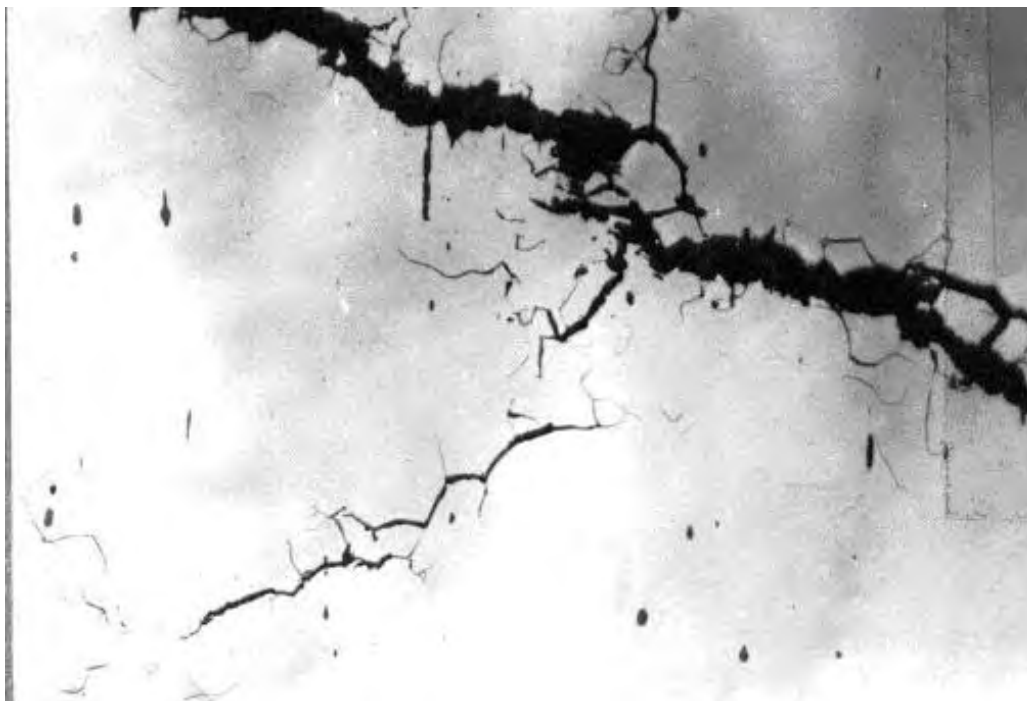


Figure 3-15-5—Photomicrograph of a crack in the tubesheet shown in Figure 3-15-4.

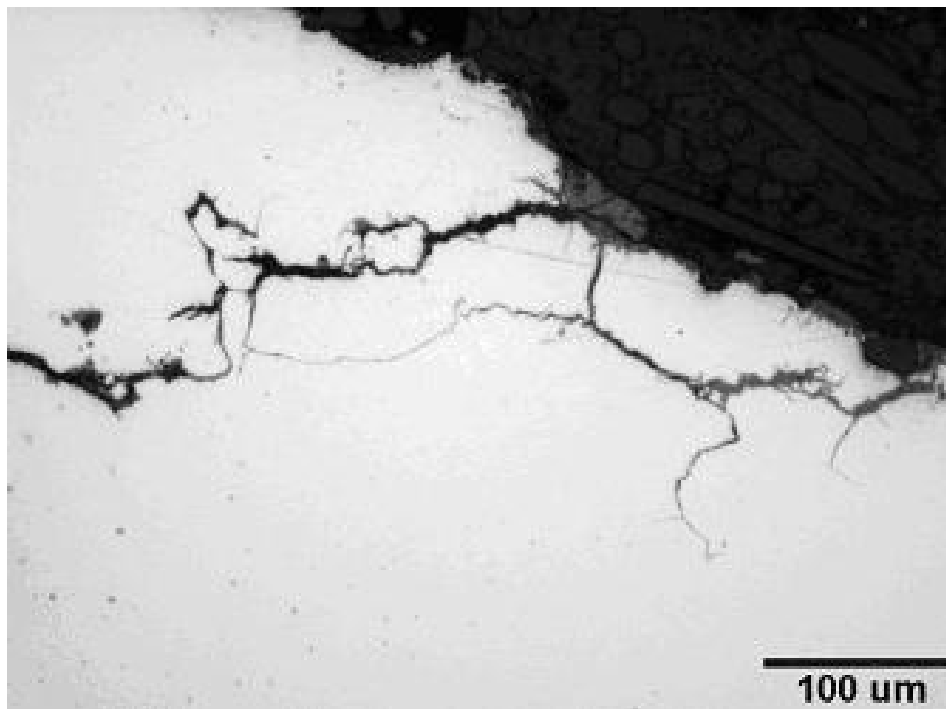


Figure 3-15-6—Photomicrograph of caustic cracking initiating on the ID of a carbon steel socket weld in non-PWHT'd piping in a suction drum downstream of a caustic scrubber. Unetched.

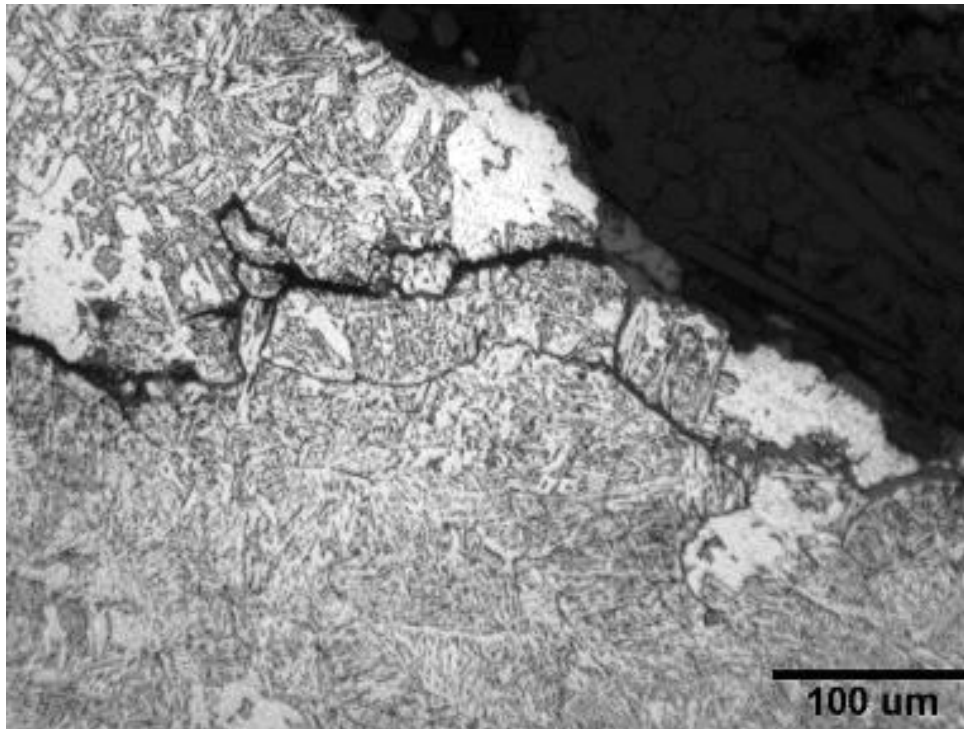


Figure 3-15-7—Figure 3-15-6 in the etched condition.



Figure 3-15-8—Stainless steel expansion bellows from a steam-driven turbine previously subjected to a caustic carryover upset condition.

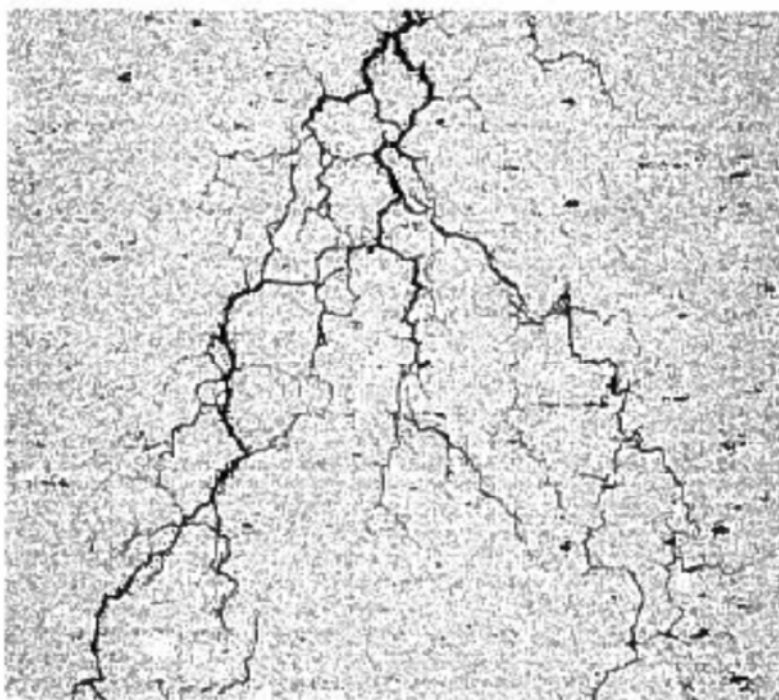


Figure 3-15-9—Micrograph showing intergranular caustic SCC in an expansion joint bellows constructed of Alloy 625 in a 400 psig steam superheater. (Reference 4)



Figure 3-15-10—Micrograph showing transgranular caustic SCC in Alloy 825. Magnification 200X. (Reference 5)

3.16 Cavitation

3.16.1 Description of Damage

- a) Cavitation is a form of wear caused by the formation and instantaneous collapse of innumerable tiny vapor bubbles.
- b) The collapsing bubbles exert severe localized impact forces that can result in metal loss. ([Figure 3-16-1](#))
- c) The bubbles may contain the vapor phase of the liquid, air, or other gas entrained in the liquid medium.

3.16.2 Affected Materials

Most common materials of construction including copper and brass, cast iron, carbon steel, low-alloy steels, 300 series SS, 400 series SS, and nickel-based alloys can be affected by cavitation, although certain materials have greater resistance than others.

3.16.3 Critical Factors

- a) In a pump, the difference between the actual pressure or head of the liquid available (measured on the suction side) and the vapor pressure of that liquid is called the net positive suction head (NPSH) available. The minimum head required to prevent cavitation with a given liquid at a given flow rate is called the NPSH required. Inadequate NPSH can result in cavitation.
- b) Temperatures approaching the boiling point of the liquid are more likely to result in bubble formation than lower-temperature operation.
- c) The presence of solid or abrasive particles is not required for cavitation damage but will accelerate the damage.
- d) Cavitation taking place in a corrosive environment can be accelerated by the corrosive effects of the environment. This is often referred to as cavitation-corrosion.

3.16.4 Affected Units or Equipment

- a) Cavitation is most often observed in pump casings, pump impellers (low-pressure side), and in piping downstream of orifices or control valves.
- b) Damage can also be found in restricted-flow passages or other areas where turbulent flow is subjected to rapid pressure changes within a localized region. Examples of affected equipment include heat exchanger tubes, venturis, and seals.

3.16.5 Appearance or Morphology of Damage

- a) Cavitation damage generally looks like sharp-edged pitting but may also have a gouged appearance in rotational components. Damage is typically localized to the cavitation zone. ([Figure 3-16-2](#) to [Figure 3-16-5](#))
- b) Cavitating pumps or downstream of control valves may sound like pebbles are tumbling or rattling inside and are typically accompanied by higher vibrations.

3.16.6 Prevention/Mitigation

- a) A mechanical modification or design or operating change is usually required in order to fix a cavitation problem. Resistance to cavitation damage may not be significantly improved by a material change. However, wear-resistant alloys and ceramic coatings can help improve cavitation resistance in some situations.
- b) Cavitation is best prevented by avoiding conditions that allow the absolute pressure to fall below the vapor pressure of the liquid. Changing the material may also help. Examples of steps that can be taken include:

1. streamlining the flow path to reduce turbulence;
 2. decreasing fluid velocities;
 3. removing entrained air;
 4. increasing the suction pressure of pumps while reviewing the pump efficiency curve;
 5. altering the fluid properties, perhaps by adding additives;
 6. using hard surfacing or hardfacing; or
 7. using a harder and/or more corrosion-resistant material.
- c) When attack is accelerated by the mechanical disruption of protective layers or films on the metal surface, such as a protective corrosion scale or inhibitor film, changing to a more corrosion-resistant material may be beneficial. However, changing to a higher hardness version of the same or a similar material in this situation may not improve cavitation resistance. In addition, excessively hard materials may not be suitable if they lack the toughness required to withstand the high local pressures and impact (shear loads) of the collapsing bubbles.

3.16.7 Inspection and Monitoring

- a) VT of suspect areas, including use of a boroscope if direct access is not available, can often identify cavitation damage. Typically, the inspection is performed during plant shutdowns.
- b) UT, including manual UT scanning and/or AUT, can be used for measuring remaining thickness at damaged areas if the damaged area is large enough and smooth enough for UT to be effective. However, since the damage is normally highly localized, it might be difficult to pinpoint the location of the damage.
1. It can be difficult to get accurate thickness readings on pump casings or other castings due to their inherent thickness variability combined with the fact that inside and outside surfaces may not be parallel.
- c) RT can be used to quantify thickness loss in affected components if accessibility allows. Pitting location and depth are measured with quantitative radiographic techniques.
- d) Acoustic monitoring of turbulent areas can detect characteristic sound frequencies associated with cavitation. The technique is a qualitative method to determine damage progression.
- e) Other techniques include monitoring of fluid properties to find locations of highly turbulent flow.

3.16.8 Related Mechanisms

Erosion and erosion-corrosion ([3.27](#)).

3.16.9 References

1. "Evaluation of Erosion and Cavitation," *Metals Handbook—Corrosion*, Volume 13, ASM International, Materials Park, OH.
2. C.P. Dillon, *Corrosion Control in the Chemical Process Industries*, Materials Technology Institute (printed by NACE), MTI Publication No 45, Second Edition, St. Louis, MO, 1994.
3. V.R. Pludek, *Design and Corrosion Control*, Macmillan Press, 1979.

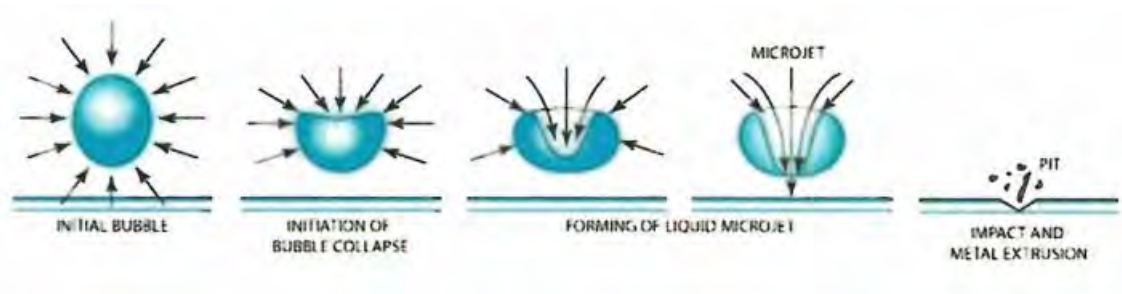


Figure 3-16-1—Mechanism of cavitation damage. As vapor bubbles collapse, microjets form that result in high forces that damage the equipment.



Figure 3-16-2—Cutaway of a CS butterfly valve with cavitation damage after 2 years of service due to a high pressure drop across the valve in a hydrocarbon drain line off a cold low-pressure separator in an atmospheric resid desulfurizing unit.



Figure 3-16-3—Closer view of the damaged surface of the butterfly valve in Figure 3-16-2.



Figure 3-16-4—Cavitation pitting on the low-pressure side of a stainless steel pump impeller.



Figure 3-16-5—Pitting caused by cavitation on the water side of a cast iron cylinder liner in a large engine.

3.17 Chloride Stress Corrosion Cracking

3.17.1 Description of Damage

Surface initiated cracking of 300 series SS and some nickel-based alloys under the combined action of tensile stress, temperature, and an aqueous chloride environment. It is also referred to as chloride cracking.

3.17.2 Affected Materials

- a) All 300 series SS are highly susceptible. Welds in 300 series SS normally contain some ferrite, producing a duplex structure that is usually more resistant to chloride stress corrosion cracking (Cl^- SCC) than the base metal.
- b) Duplex stainless steels are more resistant but still susceptible.
- c) Nickel-based alloys are highly resistant but not immune.

3.17.3 Critical Factors

- a) Chloride content, temperature, pH, tensile stress, presence of oxygen, and alloy composition are critical factors.
- b) Cl^- SCC is caused by the inorganic chloride ion (Cl^-) (or other inorganic halide ions such as bromide, in which case it might be named differently). Organic chlorides will not directly cause Cl^- SCC, but they can, and typically do, produce ionic, inorganic chlorides by the processes of hydrolysis or thermal decomposition (pyrolysis). Therefore, organic chlorides can lead to Cl^- SCC.
- c) Increasing levels of chloride increase the likelihood of cracking.
 - 1. No practical lower limit for chlorides exists because of the potential for chlorides to concentrate. For example, heat transfer conditions, as on the surface of exchanger tubes, significantly increase cracking potential. Repetitive wetting and drying situations, including alternating steam and water, can also lead to cracking.
 - 2. Non-condensing systems will be a particular concern, because the chlorides cannot be removed with the water phase.
- d) Increasing temperatures increase the potential for cracking, as long as the other required elements (stress and aqueous chloride solution) are present concurrently.
 - 1. Although there are exceptions at lower temperatures and even ambient temperature, particularly with highly cold worked or sensitized materials, cracking usually occurs at metal temperatures above about 140 °F (60 °C), and experience has shown this to be a useful temperature limit guideline for fixed equipment in the refining industry.
- e) The potential for cracking increases at lower pH; however, SCC usually does not occur at pH values below 2. At these lower pH values, uniform corrosion generally predominates. Cl^- SCC tendency decreases toward the alkaline pH region; however, stainless steels and some nickel-based alloys (e.g. Alloy 800 and Alloy 825) can suffer caustic SCC in alkaline environments. (See 3.15.)
- f) The tensile stress may be applied or residual. The most common area of concern is non-stress-relieved welds. However, highly stressed or cold worked components, such as expansion bellows, are also highly susceptible to cracking.
- g) Oxygen dissolved in the water normally accelerates SCC, but it is not clear whether there is an oxygen concentration threshold below which Cl^- SCC does not occur. Other oxidizers in addition to oxygen (e.g. CO and CO_2) can also enhance Cl^- SCC.

- h) Nickel content of the alloy has a major effect on resistance. The greatest susceptibility occurs in stainless steels with a nickel content of 8 % to 12 %.
 - 1. Alloys with nickel contents above 35 % are highly resistant, and alloys above 45 % are nearly immune in refining applications, but cracking can still occur in severe conditions.
 - 2. Low-nickel stainless steels, such as the duplex (ferrite-austenite) stainless steels, have improved resistance over the 300 series SS but are not immune.

3.17.4 Affected Units or Equipment

- a) Most non-stress-relieved 300 series SS piping and equipment in any process unit are susceptible to Cl^- SCC. Even if the process side will not cause SCC, if the piping or equipment operates above 140 °F (60 °C), it is likely exposed to alternating wet and dry conditions on the outside.
- b) Chloride cracking has occurred in water-cooled condensers and on the process side of crude tower overhead condensers.
- c) Stainless steel drains in hydroprocessing units are susceptible to cracking, particularly during start-up, if not properly purged.
- d) Bellows and instrument tubing, particularly those associated with hydrogen recycle streams contaminated with chlorides, can be affected.
- e) External Cl^- SCC can occur on insulated 300 series SS surfaces when insulation gets wet.
 - 1. The operating temperature range of most concern for external Cl^- SCC is 140 °F (60 °C) to 400 °F (205 °C).
- f) Chloride cracking has occurred in boiler drain lines.
- g) Highly localized Cl^- SCC has occurred in exchanger tube bundles where the bulk fluid temperature inside the tubes was above the water dew point. Cold fluid entering the shell side caused shock condensation within the tubes and resultant chloride cracking on the tube side.
- h) Units processing or co-processing bio-based or renewable feedstocks (biomass, natural fats and oils, etc.) are particularly susceptible to Cl^- SCC due to high levels of organic chlorides converting to inorganic chlorides in the reactor effluent.

3.17.5 Appearance or Morphology of Damage

- a) Surface-breaking cracks can occur from the process side or externally under insulation. (Figure 3-17-1 and Figure 3-17-2)
- b) The component usually shows no visible signs of corrosion.
- c) Characteristic stress corrosion cracks have many branches and may be visually detectable as spider web or craze cracking on the surface. (Figure 3-17-3)
- d) Metallography of cracked samples typically shows branched, transgranular cracks. (Figure 3-17-4 to Figure 3-17-6)
- e) Cracking of sensitized 300 series SS may be intergranular.
- f) Cl^- SCC in nickel-based alloys, which can occur under severe conditions, appears similar to Cl^- SCC in stainless steel. (Figure 3-17-7)
- g) Fracture surfaces typically have a brittle appearance.

3.17.6 Prevention/Mitigation

- a) Materials of construction resistant to Cl^- SCC should be used. Carbon steels, low-alloy steels, and 400 series SS are not susceptible to Cl^- SCC.
- b) When hydrotesting, low-chloride-content water should be used, followed quickly by thorough dryout.
- c) A suitable coating should be applied to stainless steel piping and equipment prior to insulating.
 - 1. Shrink-wrapped PVC labels, coatings, or label adhesives with high levels of chlorides or other halogen ions should be avoided.
- d) Avoid designs that create stagnant regions where chlorides can deposit or concentrate.
- e) Although not a standard or common refining industry practice, a suitable high-temperature stress relief of 300 series SS after fabrication will reduce residual stresses. However, consideration should be given to the possible effects of sensitization that may occur, increasing susceptibility to PTA SCC (3.52), possible distortion problems, and the potential for stress relaxation cracking (SRC) (3.54).
- f) Avoid exchanger designs with 300 series SS steel tubes and a high delta T between the shell and tube side where localized condensation can occur on or in the tubes.
- g) Avoid contact with high-chloride water run-off that can occur with the use of salts for snow and ice melting.

3.17.7 Inspection and Monitoring

Cracking may be either process side or external (usually under insulation that has become wet or where external water can collect), and it should be understood on which side the damage is occurring in order to properly develop an inspection plan. Cl^- SCC may be detected using the following methods.

- a) VT can be used to find advanced stages of cracking.
- b) PT can be used for Cl^- SCC. However, extremely fine cracks may be difficult to detect with PT. Special surface preparation methods, including polishing or high-pressure water blast, may be required in some cases, especially in high-pressure services.
- c) ECT inspection methods can be used on condenser tubes as well as piping and pressure vessels.
- d) Angle beam UT (SWUT and PAUT) from the opposite wall can be used for crack detection; however, detection and characterization of the cracking will be difficult due to the craze-cracked, multi-branched appearance of Cl^- SCC.
- e) RT is often not sensitive enough to detect cracks except in advanced stages where a sufficient network of cracks has developed.

3.17.8 Related Mechanisms

Caustic SCC (3.15), PTA SCC (3.52), and brine corrosion (3.10).

3.17.9 References

- 1. C.P. Dillon, *Corrosion Control in the Chemical Process Industries*, Materials Technology Institute (printed by NACE), MTI Publication No 45, Second Edition, St. Louis, MO, 1994, pp. 88–90.
- 2. *Corrosion Basics—An Introduction*, NACE International, Houston, TX, 1984, pp. 111–123.
- 3. *Focus on Chloride Stress Corrosion Cracking (CSCC) of 300 Series Stainless Steels*, MTI Technical Awareness Bulletin No. 8, Materials Technology Institute, St. Louis, MO, 2012.
- 4. D.R. McIntyre and C.P. Dillon, *Guidelines for Preventing Stress Corrosion Cracking in the Chemical Process Industries*, MTI Publication No. 15, Materials Technology Institute, St. Louis, MO, 1985.



Figure 3-17-1—External cracking of Type 304 SS instrument tubing under insulation.



Figure 3-17-2—External cracking of Type 304 SS instrument tubing under insulation.



Figure 3-17-3—Cracking on the shell side of a Type 316L SS tube in steam service at 450 °F (230 °C) showing tight cracks with a crazed or spider web appearance.



Figure 3-17-4—Photomicrograph of a cross section of the tube in Figure 3-17-3 showing fine branching cracks. (Magnification 50X, unetched.)

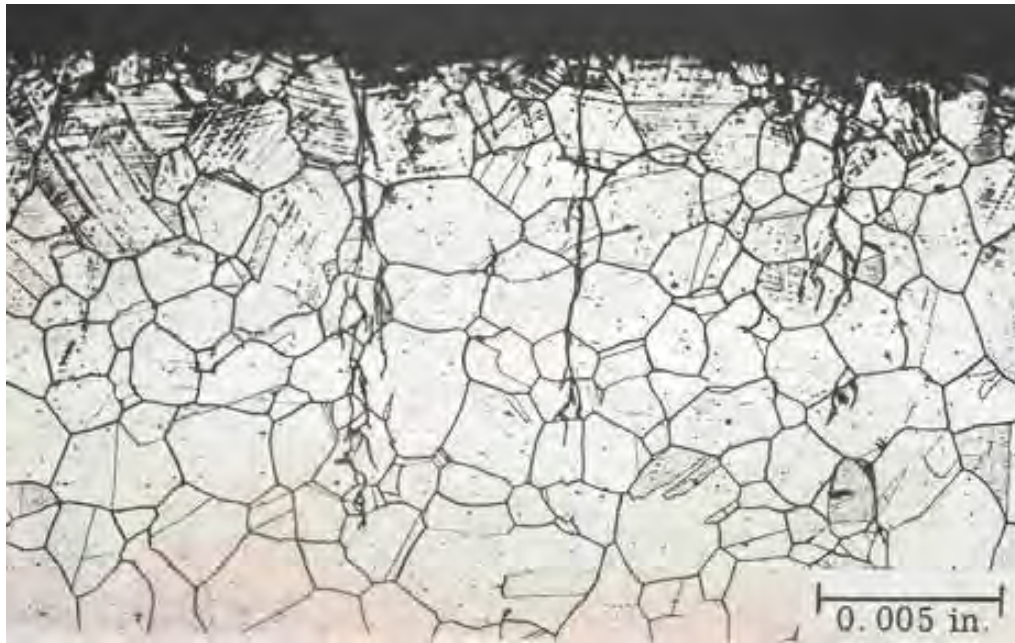
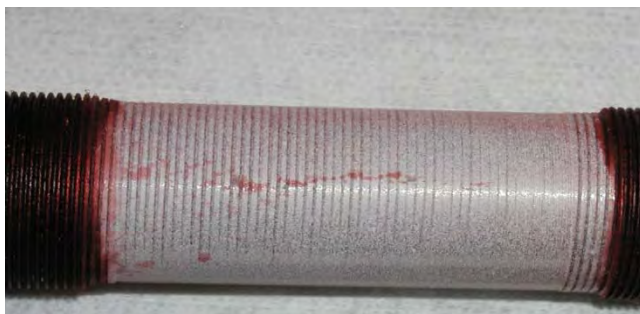


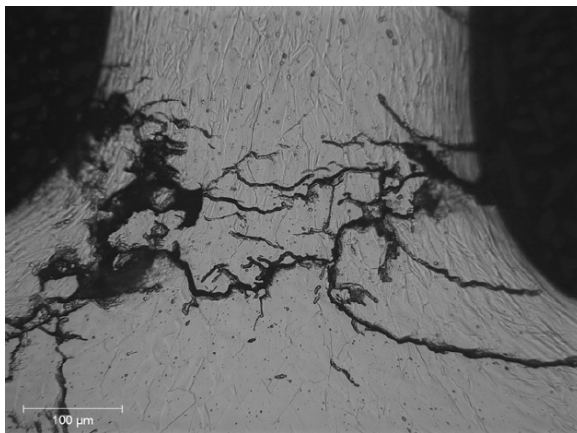
Figure 3-17-5—Another photomicrograph of a cracked tube illustrating the transgranular mode of cracking initiating at the surface. (Etched.)



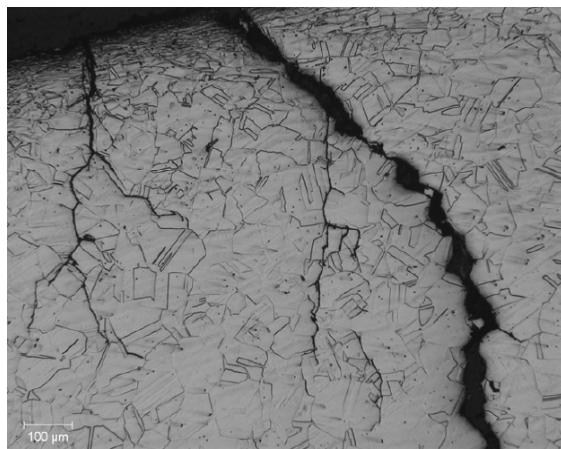
Figure 3-17-6—Cl⁻ SCC on the thread surface of a failed 303 SS bolt.



(a)



(b)



(c)

Figure 3-17-7—Severe cracking of a finned Alloy C-276 tube in a deethanizer reboiler after 8 years of service due to ammonium chloride carryover. (a) Hundreds of cracks initiated on the OD (process side) of the tube. (b) The cracks were associated with the cold-worked portion of the tubes at the fins. (c) The cracks were branching and transgranular, typical of Cl^- SCC.

3.18 CO₂ Corrosion

3.18.1 Description of Damage

CO₂ corrosion results when CO₂ dissolves in water to form carbonic acid (H₂CO₃). The acid may lower the pH, and sufficient quantities may promote general corrosion and/or pitting corrosion of carbon steel.

3.18.2 Affected Materials

Carbon steel and low-alloy steels are affected. Increasing the level of chromium in steels offers no major improvement in resistance until a minimum of 12 % Cr is reached, i.e. Type 410 SS. 300 series austenitic SS is highly resistant to CO₂ corrosion.

3.18.3 Critical Factors

- a) Liquid water must be present for CO₂ corrosion to occur. Beyond that, the partial pressure of CO₂, pH, temperature, oxygen contamination, and velocity are critical factors.
- b) Increasing partial pressures of CO₂ result in lower pH and, therefore, higher rates of corrosion.
- c) Corrosion occurs in the liquid water phase, often at locations where CO₂ condenses from the vapor phase.
- d) Increasing temperatures increase corrosion rate up to the point where CO₂ is driven off.
- e) Oxygen can accelerate corrosion rates. Oxygen should be limited to 10 ppb to avoid accelerating corrosion.
- f) High velocity and turbulence can cause accelerated, localized corrosion.

3.18.4 Affected Units or Equipment

- a) BFW and condensate systems in all units are affected.
- b) Effluent gas streams off the shift converters in hydrogen plants can be affected. Corrosion usually occurs when the effluent stream drops below the dew point at approximately 300 °F (150 °C). Corrosion rates as high as 1000 mpy have been observed.
- c) Overhead systems of regenerators in CO₂ removal plants are affected.
- d) Stripping steam is commonly used in crude towers, and so CO₂ corrosion can occur in the overhead system where the dew point is reached.
- e) Locations where high velocity, impingement, or turbulence can create increased susceptibility include areas downstream of control valves, and changes in piping direction (e.g. at elbows and tees) or piping diameter (i.e. at reducers).
- f) Corrosion may occur along the bottom surface of a pipe if there is a separate water phase or along the top surface of a pipe if condensation in wet gas systems occurs.
- g) Locations where a cooling effect can cause condensation and resultant CO₂ (carbonic acid) corrosion include where insulation is damaged, where portions of blind flanged nozzles extend beyond the insulation and thus cool below the dew point, and where pipe supports attach to piping. (Figure 3-18-1 and Figure 3-18-2)

3.18.5 Appearance or Morphology of Damage

- a) The appearance can differ depending on the unit and equipment in which it occurs (steam and condensate systems vs H₂ manufacturing units vs crude tower overheads vs CO₂ removal plants vs oilfield production equipment). Contributing to the differences in appearance are the type of water (BFW or steam condensate vs untreated fresh water vs salt water or brine) and the other species in the water, e.g. oxygen, H₂S, and other acids and salts.

- b) Localized general thinning and/or pitting corrosion normally occurs in carbon steel. (Figure 3-18-3 to Figure 3-18-5)
- c) Corrosion generally occurs or is worse in areas of turbulence and impingement. It is sometimes seen at the root of piping welds.
 - 1. Carbon steel may suffer deep pitting, grooving, or smooth “wash out” in areas of turbulence.
- d) Corrosion may initiate where water first condenses and may be most severe at water/vapor interfaces.
- e) It may appear as a number of flat-bottomed pits, sometimes called “mesa”-type pitting. (Figure 3-18-6)

3.18.6 Prevention/Mitigation

- a) Corrosion inhibitors can reduce CO₂ corrosion in steam condensate systems. Vapor phase inhibitors may be required to protect against condensing steam.
- b) Increasing condensate pH above 6 can reduce corrosion in steam condensate systems.
- c) 300 series SS are highly resistant to CO₂ corrosion in most applications. 400 series SS and duplex stainless steel are also resistant.
- d) Selective upgrading to stainless steel is usually required in operating units designed to produce and/or remove CO₂ (i.e. hydrogen plants and CO₂ removal units). Selecting a stainless steel to mitigate CO₂ corrosion in any operating unit needs to account for other potential damage mechanisms applicable to the specific environment.
- e) CO₂ corrosion in steam condensate systems can often be managed by correcting or improving the operating conditions and/or water treatment program.
- f) Ensure insulation and jacketing are in good condition to prevent unexpected and undesired cooling, which could lead to condensation and resultant CO₂ corrosion.
- g) Internal coatings can be effective where the design and environment permit.

3.18.7 Inspection and Monitoring

- a) VT, UT, and RT (preferably profile RT) can be used for general and local loss in thickness where water wetting is anticipated.
 - 1. The use of remote video probes can be effective for locations with limited or no direct line-of-sight (e.g. in boiler tubes).
- b) Preferential corrosion of welds may require angle beam UT (SWUT or PAUT) or RT.
- c) Permanently mounted thickness monitoring sensors can be used.
- d) Monitor water analyses (pH, Fe, O₂, etc.) to determine changes in operating conditions.

3.18.8 Related Mechanisms

Boiler water condensate corrosion (3.9) and carbonate cracking (3.12).

3.18.9 References

1. *Corrosion Control in the Refining Industry*, NACE Course Book, NACE International, Houston, TX, 1999.
2. L. Garverick, *Corrosion in the Petrochemical Industry*, ASM International, Materials Park, OH, 1994.
3. H.M. Herro and R.D. Port, *The Nalco Guide to Cooling Water System Failure Analysis*, McGraw-Hill, New York, NY, 1991, pp. 259–263.



Figure 3-18-1—CO₂ corrosion caused a leak in an elbow at a support leg. The cooling effect of the support leg caused carbonic acid to condense from the vapor phase.



Figure 3-18-2—Corrosion found on the inside of the elbow in Figure 3-18-1.



Figure 3-18-3—CO₂ corrosion of a carbon steel oil and gas production flow line.

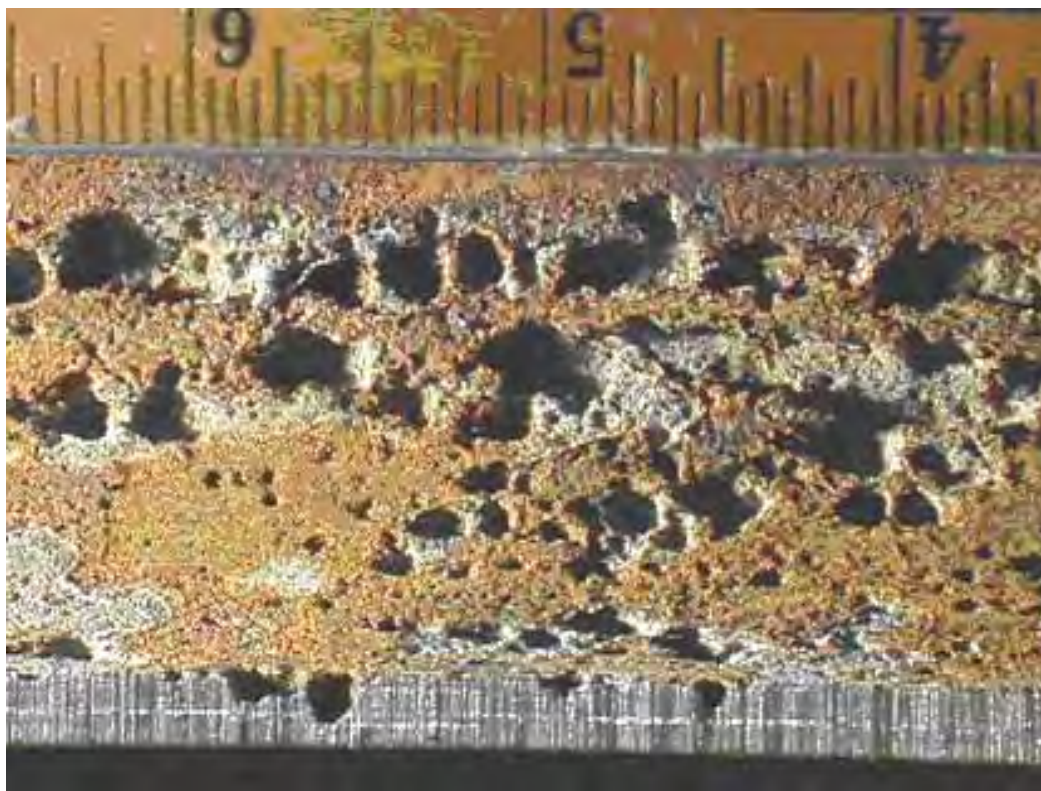


Figure 3-18-4—Higher-magnification view of the corrosion pits in Figure 3-18-3.



Figure 3-18-5—CO₂ corrosion of a carbon steel pipe nipple in CO₂-contaminated water.

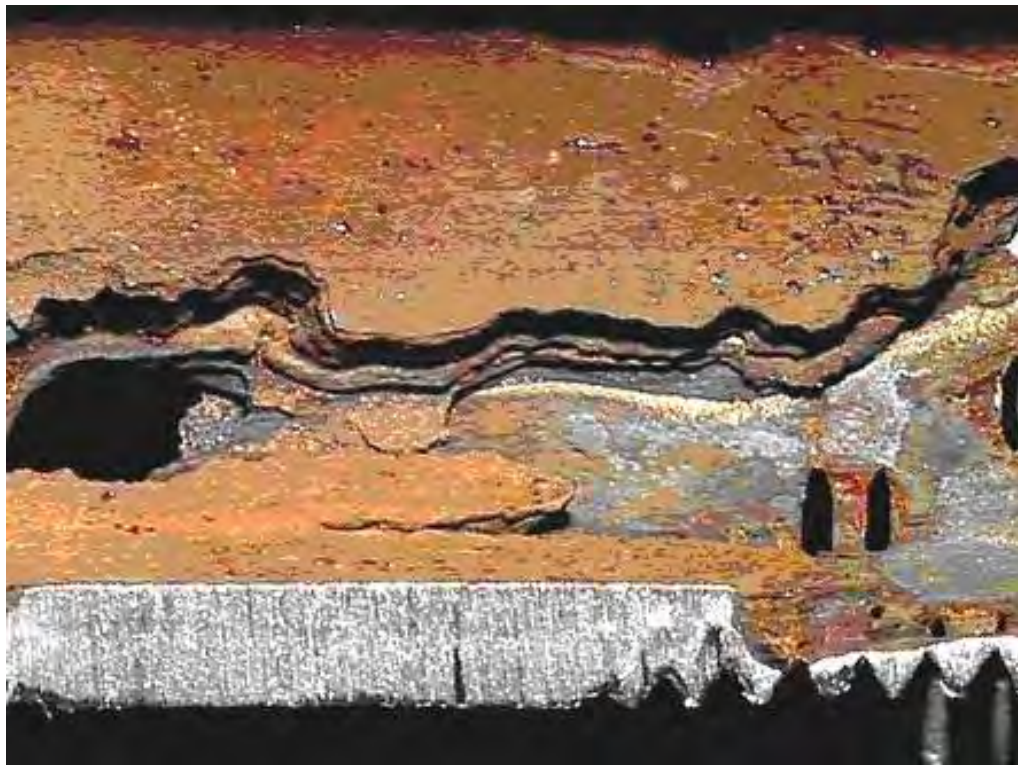


Figure 3-18-6—A view inside the nipple in Figure 3-18-3 showing “mesa”-type corrosion.

3.19 Concentration Cell Corrosion

3.19.1 Description of Damage

Concentration cell corrosion is not a separate corrosion mechanism but rather provides an explanation for or has an influence on a number of commonly occurring corrosion phenomena, including under-deposit corrosion, crevice corrosion, contact point corrosion (also called touch point corrosion), soil/air interface corrosion (see 3.57), and CUI (see 3.22).

3.19.2 Affected Materials

Susceptibility to concentration cell corrosion correlates to the overall aqueous corrosion resistance of the material. Carbon steel is the most susceptible and the most commonly used material in the situations where these phenomena occur in refining. Low-alloy steels and stainless steels are also susceptible, with degree of susceptibility depending on the chemical composition of the alloy and the aggressiveness of the environment. Higher-alloy materials including high-Cr ferritic stainless steels, austenitic super stainless steels, super duplex stainless steels, and Ni-Cr-Mo alloys, as well as titanium and its alloys, have good to excellent resistance to concentration cell corrosion in refining applications.

3.19.3 Critical Factors

- a) Concentration cell corrosion occurs in aqueous environments. It involves an *occluded cell* surrounded by an environment with a slightly different composition. The occluded cell is the area beneath the deposit, inside the crevice, where the pipe sits on its support, the first few inches of soil beneath the ground surface, or where pipe is contacted by wet insulation. In most cases, the difference between the environment in the occluded cell and the area around it is the oxygen concentration. Because the oxygen within the occluded cell gets depleted by the initial corrosion that occurs, the area outside the occluded cell has a higher oxygen concentration than that within the occluded cell. This *differential aeration cell*, or *oxygen concentration cell*, causes the lower-oxygen area to corrode preferentially to the higher-oxygen area. It is essentially a galvanic couple where the low-oxygen area is the anode and the higher-oxygen area is the cathode.
- b) Concentration cell corrosion can also occur in the absence of air or oxygen, such as under deposits laying at the bottom of a tower or vessel, or along the bottom of a horizontal run of piping in a refinery process unit where there is presumably no air or oxygen present during operation. In this case, if there is under-deposit corrosion, it is due to a chemical species other than oxygen, perhaps sulfur or chlorides.
- c) Crevice corrosion in 300 series SS and similar alloys is related to the chloride content of the environment as well as the pH and temperature. It is closely related to the chloride pitting phenomenon in these materials. In addition to a contribution from the differential aeration cell created between the area within the crevice and the area outside it, the pH within the crevice decreases as the corrosion proceeds, by a process called metal ion hydrolysis, thereby further accelerating the corrosion rate.
 1. Resistance to chloride crevice corrosion (and chloride pitting) of stainless steels is related to the amount of Cr and Mo, as well as certain other chemical additions, in the alloy. It is typically represented by the PREN, which quantifies the material's expected resistance based on chemical composition. [See *Brine Corrosion* (3.10) for further discussion of PREN.]
- d) In order for concentration cell corrosion to occur, a potentially corrosive aqueous environment must exist. The presence of a concentration cell generally accelerates the corrosion that would otherwise occur at a slower rate without the concentration cell, in the same way that a galvanic couple accelerates the corrosion on the more anodic material when placed in a potentially corrosion-causing environment but does not create a new corrosion mechanism by itself. The corrosion rate under the deposit or within the crevice occurs at an accelerated rate compared to the corrosion occurring outside the deposit or crevice. The corrosion at the contact point where the pipe sits on its support is accelerated compared to the atmospheric (and water) corrosion occurring on the rest of the pipe. The soil corrosion at the soil/air interface is accelerated by the oxygen differential between the first few inches of soil and the air above it. If there is no corrosive environment within and surrounding the occluded cell, e.g. in clean, water-free hydrocarbon, there will not be corrosion beneath any deposits, either (assuming no MIC). Similarly, even corrosive salt deposits such as ammonium

chloride will not cause corrosion until they become water-wet and thereby create an acidic, corrosive environment beneath the deposit.

3.19.4 Affected Units or Equipment

- a) All process and utility piping and equipment in a refinery is potentially susceptible to concentration cell corrosion, either on the inside, the outside, or both.
- b) Anywhere deposits (sludge, scale, salts, etc.) form within the piping or equipment is a potential site for under-deposit corrosion.
- c) Equipment internals that are bolted together, e.g. tray components in towers, as well as baffle holes through which tubes pass in heat exchangers, flange and gasket faces, and close-fitting components in valves and instruments are potential locations where crevice corrosion might occur.
- d) Deposits forming on the outside of piping or equipment, e.g. dirt piling up beneath low lying piping or sloughing off of road crossings and then covering exposed bare pipe running beneath the crossing, can lead to under-deposit corrosion, which, in this example, could also be categorized as soil corrosion or soil/air interface corrosion.
- e) Loose, peeling coatings can trap moisture, dirt, or other debris and create an under-deposit or crevice corrosion condition.
- f) Everywhere a pipe is supported by a saddle, sits on a beam, or is not in some way supported using a method to preclude contact point corrosion is a potential site for accelerated atmospheric corrosion. The situation is made worse if dirt or other materials can get trapped and contained within the contact area.
- g) See also ammonium bisulfide corrosion (3.5), ammonium chloride corrosion (3.6), atmospheric corrosion (3.8), brine corrosion (3.10), cooling water corrosion (3.20), CUI (3.22), fuel ash corrosion (3.30), galvanic corrosion (3.31), MIC (3.45), oxygenated water corrosion (3.49), soil corrosion (3.57), and SW corrosion (acidic) (3.58).

3.19.5 Appearance or Morphology of Damage

As with most corrosion situations in refining, concentration cell corrosion will typically result in an unevenly corroded surface often described as pitting. Crevice corrosion in austenitic stainless steels due to chlorides is typically an accumulation of sharp, narrow, deep pits. See the mechanisms in 3.58.4 g), above, for more specific descriptions.

3.19.6 Prevention/Mitigation

- a) Most situations dictate that an upgrade of material, most commonly from carbon steel, is not a practical or economic alternative.
- b) Keeping dirt and other deposits from building up against or beneath equipment will prevent this type of attack.
- c) Taking practical steps to minimize deposit, sludge, and scale formation in operating units will mitigate the damage.
- d) Pipe supports can be designed to eliminate the ability to trap dirt and moisture between the pipe and its support, e.g. by using fully welded contact points.
- e) Coatings can be used to protect steel equipment likely to become exposed to dirt or other debris buildup.
- f) Peeling coatings should be repaired.

- g) Where a materials upgrade is a reasonable solution to a crevice corrosion or under-deposit corrosion concern, e.g. where 300 series SS is commonly used or where process salt deposits are a concern, consider an upgrade to an appropriate, more corrosion-resistant alloy.

3.19.7 Inspection and Monitoring

- a) VT is the method most commonly used when access to the corroded surface is available. Pit gaging is often applied along with VT to measure the depth of the attack. Laser scanning and/or structured white light imaging with pit gages can also be performed.
- b) UT thickness measurements from the surface opposite the attack can be used to measure remaining wall thickness.
- c) UT scanning methods (e.g. AUT, manual close-grid, scanning UT) may be needed to assess large surfaces such as the bottom of a tower or vessel, i.e. by scanning from the underside to determine the amount of damage caused by deposits on the inside. Short-range (high-frequency) GWT techniques may also be used to detect wall loss.
- d) If the cause of the corrosion cannot be eliminated, permanently mounted thickness monitoring sensors can be used.
- e) The presence of deposits in heat exchangers can sometimes be detected by an increase in pressure drop or if the thermal performance of exchangers has deteriorated.

3.19.8 Related Mechanisms

Ammonium bisulfide corrosion (3.5), ammonium chloride corrosion (3.6), atmospheric corrosion (3.8), brine corrosion (3.10), cooling water corrosion (3.20), CUI (3.22), fuel ash corrosion (3.30), galvanic corrosion (3.31), MIC (3.45), oxygenated water corrosion (3.49), soil corrosion (3.57), and SW corrosion (acidic) (3.58).

3.19.9 References

None.

3.20 Cooling Water Corrosion

3.20.1 Description of Damage

General or localized corrosion of carbon steels and other metals caused by dissolved salts, gases, organic compounds, or microbiological activity in cooling water systems.

3.20.2 Affected Materials

Carbon steel, all grades of stainless steel, copper and copper alloys, aluminum and aluminum alloys, titanium, and nickel alloys.

3.20.3 Critical Factors

- a) Cooling water corrosion, fouling, and MIC are closely related and should be considered together. Fluid temperature, type of water (fresh, brackish, or salt water) and the type of cooling system (once-through, open circulating, or closed circulating), oxygen content, and fluid velocities are critical factors.
- b) Higher cooling water temperature causes increased corrosion rates.
 - 1. Increasing cooling water heat exchanger outlet temperatures and or process-side inlet temperatures tend to increase exchanger bundle corrosion rates as well as fouling tendency. If the process-side temperature is above 140 °F (60 °C), a scaling potential exists with fresh water and becomes more likely as process temperatures increase and as cooling water inlet temperatures rise. Brackish and salt water outlet temperatures above about 115 °F (45 °C) may cause serious scaling.
- c) Increasing oxygen content tends to increase carbon steel corrosion rates.
- d) Fouling may be caused by mineral deposits (hardness), silt, suspended organic materials, corrosion products, mill scale, and marine and microbiological growth.
- e) Low velocities can promote increased corrosion. Velocities should be high enough to minimize fouling and dropout of deposits but not so high as to cause erosion. Velocity limits depend on the pipe diameter or heat exchanger tube material and water quality.
 - 1. Oversized channel heads, water side exchanger shells, or dead-legs can be areas of low or stagnant flow.
 - 2. Generally, velocities below about 3 fps (1 m/s) are likely to result in fouling, sedimentation, and increased corrosion in fresh and brackish water systems. Accelerated corrosion can also result from dead spots or stagnant areas if cooling water is used on the shell side of condensers/coolers rather than the preferred tube side.
- f) High velocities can also lead to accelerated corrosion.
 - 1. Exchanger tubes can see a dramatic increase in flow velocity.
- g) 300 series SS, depending on the specific alloy and the water and metal temperatures, can suffer pitting and crevice corrosion. At temperatures above about 140 °F (60 °C), 300 series SS can also suffer Cl⁻ SCC even in freshwater systems where a chloride salt concentrating mechanism is in place. This is a particular concern with the tubes in water-cooled heat exchangers, i.e. condensers and coolers. (See [3.17](#).)
- h) Brass (Cu-Zn) alloys can suffer dezincification in fresh, brackish, and salt water systems. They can also suffer SCC if any ammonia or ammonium compounds are present in the water or on the process side if cross-leakage occurs.
- i) ERW carbon steel pipe or exchanger tubes may suffer severe weld and/or HAZ corrosion in fresh or brackish water.

- j) When connected to a more anodic material, titanium may suffer severe hydriding embrittlement. Generally, the problem occurs at temperatures above 165 °F (75 °C). (See 3.66.)

3.20.4 Affected Units or Equipment

Cooling water corrosion is a concern with cooling towers, piping, pumps, water-cooled heat exchangers, and any other equipment associated with cooling water systems.

3.20.5 Appearance or Morphology of Damage

- a) Cooling water corrosion can result in many different forms of damage including general corrosion, pitting corrosion (Figure 3-20-1), MIC, SCC, and fouling.
- b) General or uniform corrosion of carbon steel occurs when dissolved oxygen is present. Many oxidizing biocides also increase this tendency.
- c) Localized corrosion may result from under-deposit corrosion, crevice corrosion, or MIC.
- d) Wavy or smooth corrosion at nozzle inlets or outlets and exchanger tube inlets may be due to flow accelerated corrosion, erosion, or abrasion.
- e) Corrosion at ERW weld areas will appear as grooving along the weld fusion lines.

3.20.6 Prevention/Mitigation

- a) Cooling water corrosion (and fouling) is best managed by proper design, operation, and chemical treatment of cooling water systems.
- b) Process-side inlet temperatures of water-cooled exchangers should be maintained below 140 °F (60 °C).
- c) Minimum and maximum water velocities must be maintained, particularly in saltwater systems.
- d) The metallurgy of heat exchanger components may need to be upgraded for improved resistance, especially in waters with high chloride content, low velocity, and/or poorly maintained water chemistry, where exchanger process-side temperatures are high, or where there is simply the desire to extend tube life.
- e) Periodic mechanical cleaning of tube IDs and ODs should be performed in order to maintain clean heat transfer surfaces.
- f) With very few exceptions, cooling water should be on the tube side to minimize stagnant areas.
- g) Installation of sacrificial anodes on the cooling water side of water-cooled heat exchangers can increase the life of channel heads, tubesheets, and tubes to a certain extent, as long as they are galvanically coupled to the anodes.

3.20.7 Inspection and Monitoring

- a) Cooling water should be monitored for process conditions that affect corrosion and fouling, including but not limited to:
 - 1. pH,
 - 2. oxygen content,
 - 3. cycles of concentration,
 - 4. biocide and other chemical residual,

5. biological activity,
 6. iron and manganese count,
 7. cooling water outlet temperatures,
 8. hydrocarbon contamination, and
 9. process leaks.
- b) Periodic calculation of overall heat exchanger performance (U-factors) will provide information on potential scaling and fouling. These could be an indication that corrosion damage is occurring in the piping, exchanger tubes, and/or other equipment in the system.
 - c) Strategically placing continuous corrosion monitoring devices on the system, such as corrosion coupons, ER probes, or online monitoring sensors, can provide an early indication of increased corrosion rates that need further evaluation.
 - d) Areas with sharp reduction or large increases in diameter should be considered for velocity survey locations as velocities that are either too high or too low can dramatically affect the damage rate of the equipment. Several types of flow meters are available that can be used to check the velocity of water in the cooling water system.
 - e) When water sides of exchangers are opened for inspection, checking the sacrificial anodes (when installed) may indicate the relative corrosivity of the cooling water and if the sacrificial anode has been consumed and needs replacement.
 - f) Exchanger tube inspection can be used to establish corrosion rates and predict tube life in order to plan for tube or tube bundle repair/replacement. Some nondestructive methods to inspect tubes are as follows.
 1. RFT is commonly used for inspection of ferrous (carbon steel) tubes. RFT has an equal sensitivity to ID and OD indications and can detect and size corrosion and pitting as well as baffle cuts.
 2. ECT is the preferred method for non-ferromagnetic materials as it has a higher probability of detecting all types of damage than ultrasonic methods.
 3. IRIS is used when a higher flaw detection and sizing capability is needed (compared to the other methods), but it is slower, and thorough tube cleaning is required prior to inspection. IRIS can be used on both ferrous and non-ferrous materials. IRIS is most commonly used on carbon steel tubes.
 - g) A destructive method for evaluation is extracting and splitting representative tubes to gain access to the internal surfaces for direct examination. This method is most often used on failed tubes that require replacement and is useful in determining the cause of the tube failure. It may also be used on tubes where significant damage has been indicated and needs verification. The knowledge gained from this method may aid in tube material selection and can help create mitigation plans to avoid future damage.

3.20.8 Related Mechanisms

Microbiologically induced corrosion (3.45), Cl^- SCC (3.17), galvanic corrosion (3.31), concentration cell corrosion (3.19), and brine corrosion (3.10).

3.20.9 References

1. T.J. Tvedt, Jr., "Cooling Water Systems," *Corrosion Control in the Refining Industry*, NACE Course Book, NACE International, Houston, TX, 1999.
2. H.M. Herro and R.D. Port, *The Nalco Guide to Cooling Water System Failure Analysis*, McGraw-Hill, New York, NY, 1991, pp. 259–263.

3. NACE SP0189, *Online Monitoring of Cooling Water Systems*, NACE International, Houston, TX.
4. NACE SP0300, *Corrosion of Metals and Alloys—Corrosion and Fouling in Industrial Cooling Water Systems—Part 1: Guidelines for Conducting Pilot-scale Evaluation of Corrosion and Fouling Control Additives for Open Recirculating Cooling Water Systems*, NACE International, Houston, TX.
5. NACE/EFC Joint Publication, *Monitoring and Adjustment of Cooling Water Treatment Operating Parameters*, NACE International, Houston, TX.

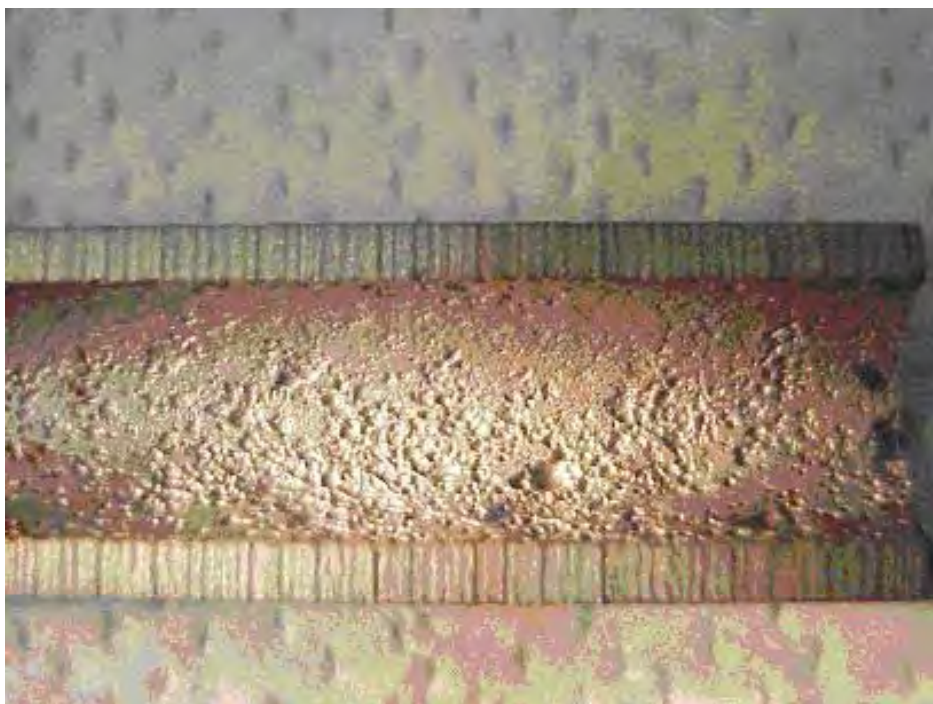


Figure 3-20-1—Cooling water corrosion on the ID of a carbon steel heat exchanger tube operating at 85 °F (30 °C).

3.21 Corrosion Fatigue

3.21.1 Description of Damage

A form of fatigue cracking in which cracks develop under the combined effects of cyclic loading and corrosion. The number of fatigue stress cycles to failure is reduced in a corrosive environment as compared to the number of cycles to failure in the absence of a corrosive environment. Cracking often initiates at a stress concentration such as a pit in the surface. Cracking can initiate at multiple sites.

3.21.2 Affected Materials

All metals and alloys.

3.21.3 Critical Factors

- a) The critical factors are the same as those associated with mechanical fatigue (3.43), i.e. cyclic stress level, number and frequency of stress cycles, stress concentration, and material properties, along with the addition of the nature of the corrosive environment.
- b) Although corrosion fatigue can occur in the absence of visible or obvious corrosion on the metal surface, in practice, cracking is more likely to occur in environments that promote pitting or localized corrosion.
- c) Corrosion fatigue cracking can result from either mechanically induced cyclic stresses or thermally induced cyclic stresses. (See *Mechanical Fatigue*, 3.43, and *Thermal Fatigue*, 3.64.)
- d) Contrary to the case with purely mechanical fatigue, there is no endurance limit with corrosion fatigue. Corrosion promotes failure at a lower stress and fewer number of cycles than the materials' normal endurance limit in the absence of corrosion and often results in propagation of multiple parallel cracks.
- e) Crack initiation typically occurs at stress concentration locations such as corrosion pits, notches, surface defects, changes in section, or welds, especially fillet welds.

3.21.4 Affected Units or Equipment

Rotating equipment, deaerators, and cycling boilers as well as any equipment subjected to cyclic stresses in a corrosive environment are potentially susceptible to corrosion fatigue cracking. Some examples include the following.

- a) Rotating equipment.

Pump shafts that are not resistant to corrosion in their environment may suffer pitting or other corrosion that will reduce the fatigue life of the shaft. The pitting can act as a stress riser to promote cracking. Galvanic couples between the impeller and the pump shaft may exacerbate the problem. If any other cracking mechanisms such as SCC or SSC are involved, fatigue life may be further reduced.

- b) Deaerators.

In the late 1980s, deaerators in the pulp and paper, refining, petrochemical, and fossil fuel utility industries had major deaerator cracking problems. Cracking is typically associated with welds, especially non-stress-relieved welds, and particularly attachment welds. Complete vessel failures in the pulp and paper industry resulted in a diligent inspection program that found major cracking problems across the various industries. It was concluded that residual welding and fabrication stresses, stress risers (attachments and weld reinforcement), and the normal deaerator environment could produce multiple corrosion fatigue cracking problems.

c) Cycling boilers.

A cycling boiler may see several hundred cold starts over its useful life, which—because of differential expansion—continually cracks the protective magnetite scale, allowing corrosion to continue. This could be described as a case of low-cycle corrosion fatigue as well as cyclic stress enhanced corrosion. It is also referred to as stress-assisted cracking in some references.

d) Other equipment.

While virtually all equipment used in a refinery is subject to corrosion, even if it is only atmospheric corrosion, it is not useful in a practical sense to differentiate in most cases between corrosion fatigue and either mechanical fatigue or thermal fatigue. Most fatigue situations arising in refining can be dealt with by considering the situation as either mechanical fatigue or thermal fatigue, as applicable, without introducing the additional complicating (and mainly academic in this case) issue of corrosion fatigue. Another way of saying this is that all fatigue cracking in a refinery is corrosion fatigue, but unless there is a key contributing factor such as SCC or deep sharp pitting involved, practitioners will generally deal with the situation simply as either mechanical fatigue or thermal fatigue. In most cases, even without any contribution from corrosion, the mechanical or thermal fatigue cracking was going to occur anyway.

3.21.5 Appearance or Morphology of Damage

- a) The fatigue fracture surface will appear brittle, and the cracks will be relatively straight, transgranular, and unbranched. There may be multiple parallel cracks.
- b) Fatigue cracking will be evidenced by very little plastic deformation except that final fracture may occur by mechanical overload accompanied by plastic deformation.
- c) In rotating equipment, cracking is generally straight and transgranular with minimal branching.
- d) In deaerators and deaerator storage tanks, cracking is surface breaking to the interior of the vessel. The cracks may or may not be tight in appearance and may be tightly filled with corrosion by-products. Pitting is often a precursor to and the initiation site for cracking.
- e) In cycling boilers, the damage usually appears first on the water side of buckstay (structural) attachments. (Figure 3-21-1 to Figure 3-21-5) The cracking pattern may be circular cracks surrounding the weld between the buckstay attachment and the waterwall tube. (Figure 3-21-4) In cross section, the cracks tend to be bulbous with numerous lobes. (Figure 3-21-2 and Figure 3-21-5) The crack tips themselves may be somewhat blunted and are oxide filled and transgranular. (Figures 3-21-2, 3-21-3, and 3-21-5)
- f) In sulfiding environments, cracks will have a similar appearance to non-sulfiding environments but will be filled with a sulfide scale.

3.21.6 Prevention/Mitigation

a) Rotating equipment.

1. Select an appropriate corrosion-resistant material.
2. Protect the component from corrosion using a coating, if applicable.
3. Modify the corrosive environment by using a corrosion inhibitor, if applicable
4. Minimize galvanic couple effects.

b) Deaerators.

1. Ensure the use of proper feedwater and condensate chemical control.

2. Minimize residual welding and fabrication stresses by using PWHT.
3. Minimize weld reinforcement stress concentrators by grinding weld contours smooth.

c) Cycling boilers.

1. Start up slowly to minimize differential expansion strains.
2. Ensure proper boiler water chemistry control at all times, including start-up.

3.21.7 Inspection and Monitoring

a) Rotating equipment.

1. VT as well as UT, PT, and MT techniques can be used for crack detection.

b) Deaerators.

1. Many of the cracks are very tight and difficult to detect. Inspection should focus on welds.
2. WFMT is the most widely used off-line detection method, especially where cracks are tightly filled with corrosion by-products. It may be necessary to remove internal fixtures to gain access to fillet and other welds for WFMT.
3. Angle beam UT (SWUT or PAUT) can be used to detect cracks from the OD; however, tightly filled cracks can be difficult to detect with UT.
4. ACFM or other eddy current techniques, including phase sensitive eddy current, can detect surface-breaking cracks on the ID surface where the cracks initiate.
5. PT can be used to detect cracks; however, it is highly dependent upon surface preparation, and tightly filled cracks may preclude detection. Long penetrant and developer dwell times may be needed.
6. Online cracking examinations are often limited due to process temperature and component configuration/geometry but may include advanced ultrasonic examinations techniques such as PAUT.

c) Cycling boilers.

1. The first sign of damage is usually a pinhole leak on the cold side of a waterwall tube at a buckstay attachment.
2. Highly stressed regions in the boiler where cracking can occur can be inspected using angle beam UT (SWUT or PAUT) or EMAT techniques.
3. Cracking may occur at the membranes in the highly stressed regions, particularly corners at buckstays.

3.21.8 Related Mechanisms

Mechanical fatigue (3.43), thermal fatigue (3.64), and boiler water and condensate corrosion (3.9).

3.21.9 References

1. *Steam—Its Generation and Use*, 40th Edition, Babcock and Wilcox, 1992.
2. *Combustion: Fossil Power Systems*, Third Edition, Combustion Engineering, Windsor, CT, 1981.
3. H. Thielsch, *Defects and Failures in Pressure Vessels and Piping*, Krieger Publishing, Malabar, FL, 1977.

4. R.D. Port and H.M. Herro, *The Nalco Guide to Boiler Failure Analysis*, McGraw-Hill, New York, NY, 1991.
5. D.N. French, *Metallurgical Failures in Fossil Fired Boilers*, John Wiley and Sons, New York, NY, 1993.
6. B. Dooley and W. McNaughton, *Boiler Tube Failures: Theory and Practice*, 3 Volumes, EPRI, 1995.
7. *ASM Handbook—Materials Characterization*, Volume 10, ASM International, Materials Park, OH.
8. API Technical Report 938-C, *Use of Duplex Stainless Steels in the Oil Refining Industry*, American Petroleum Institute, Washington, DC.
9. NACE SP0590, *Prevention, Detection, and Correction of Deaerator Cracking*, NACE International, Houston, TX.



Figure 3-21-1—Corrosion fatigue failure of a boiler tube.

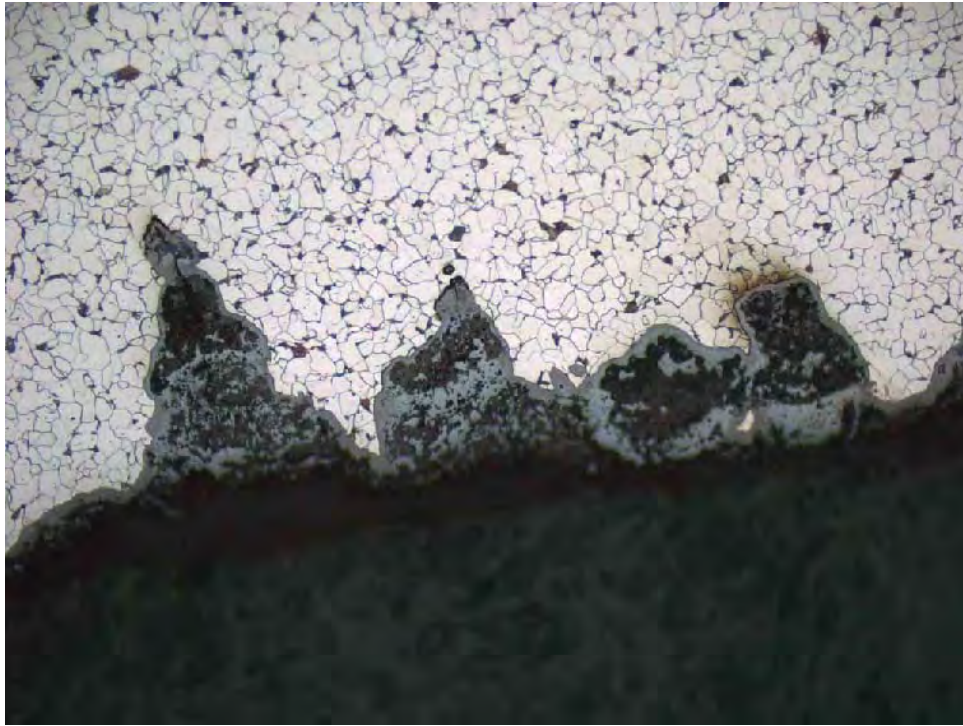


Figure 3-21-2—Metallographic mount of sample taken from failed boiler tube in Figure 3-20-1.

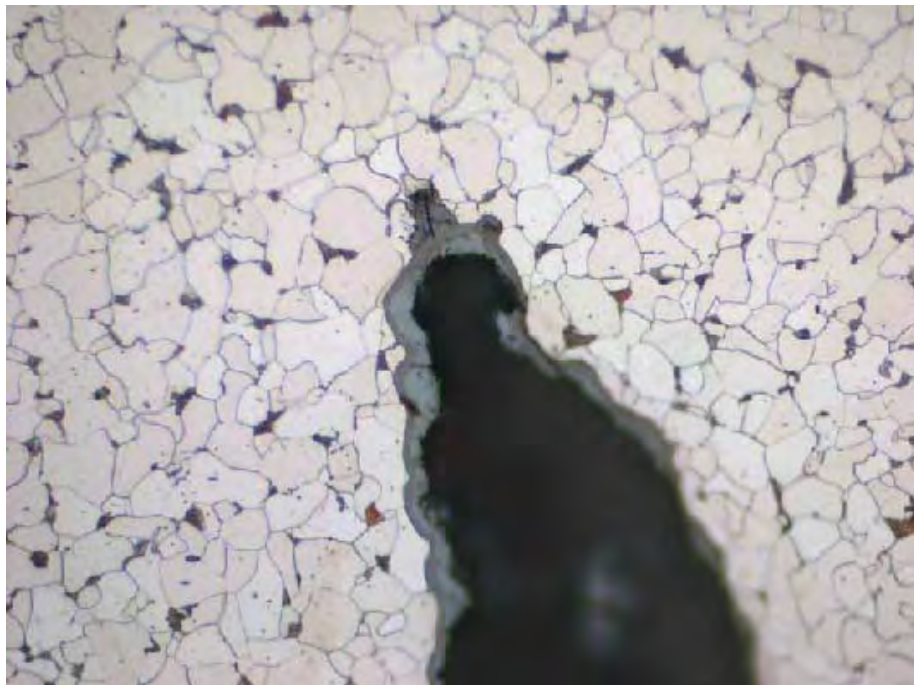


Figure 3-21-3—Higher-magnification view of sample shown in Figure 3-20-2.



Figure 3-21-4—Photograph of a carbon steel boiler tube cut in half lengthwise. Corrosion fatigue cracks initiated at the ID of the tube, opposite a buckstay attachment on the OD. (Magnification 1X.)



Figure 3-21-5—Photomicrograph showing the crack morphology that is rounded with multiple lobes and may branch to form "rabbit ears." (Magnification 25X, etched.)

3.22 Corrosion Under Insulation

3.22.1 Description of Damage

Corrosion of piping, pressure vessels, and structural components resulting from water trapped under insulation or fireproofing.

3.22.2 Affected Materials

Carbon steel, low-alloy steels, 300 series SS, 400 series SS, and duplex stainless steels.

3.22.3 Critical Factors

- a) Temperature, duration of wetting, design of the insulation system, insulation type, and environment are critical factors.

Corrosion rates increase with increasing metal temperature up to the point where the water evaporates quickly. While water boils or steams off above the boiling temperature, 212 °F (100 °C), it does not do so instantaneously. It takes some amount of time for water to boil off and wet insulation to dry out. During this time, the metal is corroding. The higher the temperature above the boiling point, the faster the water will evaporate and the insulation will dry out. However, with a high enough rate of wetting and replenishment of the water in the wet insulation, CUI can occur on equipment operating at virtually any temperature of practical concern in refining.

1. In most situations, and as a practical matter, refiners generally focus their CUI management efforts on insulated carbon steel, low-alloy steel, and 400 series SS equipment operating between 10 °F (–12 °C) and 350 °F (175 °C).
 2. For 300 series SS, where Cl[–] SCC is the concern, refiners generally focus on the temperature range of 140 °F (60 °C) to 350 °F (175 °C).
 3. For duplex stainless steel, where Cl[–] SCC is the concern, refiners generally focus on the temperature range of 280 °F (140 °C) to 350 °F (175 °C).
- b) The extent of CUI attack depends on the total amount of time the equipment remains wet from exposure to wet insulation. Therefore, while a higher operating temperature will result in a higher corrosion rate, the total amount of attack over a long period of time may occur at a lower temperature if the metal remains wet for significantly longer periods of time at the lower temperature. This is one of the reasons why CUI corrosion rates are difficult to predict.
- c) Poor design or installation of insulation systems that allow water to become trapped will increase CUI.
- d) Insulating materials that wick moisture can hold water and be more prone to causing extensive CUI.
- e) Insulating materials that dry out slowly can be more prone to causing extensive CUI.
- f) Cyclic thermal operation or intermittent service can increase corrosion.
- g) Equipment that operates below the water dew point tends to condense water on the metal surface, thus providing a wet environment and increasing the risk of corrosion.
- h) Damage is aggravated by contaminants that may be leached out of the insulation, such as chlorides.
- i) Plants located in areas with high annual rainfall or warmer marine locations are more prone to CUI than plants located in cool and dry or warm and dry locations.
- j) Environments that provide airborne contaminants such as chlorides (e.g. from marine environments or cooling tower drift) or SO₂ (e.g. from stack emissions) can accelerate corrosion.

3.22.4 Affected Units or Equipment

- a) All insulated piping and equipment are susceptible to CUI under the conditions noted above, even piping and equipment where the insulation system appears to be in good condition and no visual signs of corrosion are present.
- b) Examples of locations where CUI can occur are listed below.
 - 1. CUI can be found on equipment with damaged insulation, insulation jacketing, vapor barriers, weatherproofing or mastic, or where caulking has hardened, separated, or is missing.
 - 2. CUI can occur where water gains access at protrusions through the insulation or at insulation termination points such as flanges.
 - 3. Piping components and locations that are particularly susceptible include dead-legs (vents, drains, and other similar items), pipe hangers and other supports, valves and fittings with irregular insulation surfaces, bolted-on pipe shoes, steam tracing tube or heat tracing wire penetrations, at the terminations of insulation at flanges or other piping components, at the termination of insulation in vertical pipe, and the first few feet of a horizontal pipe run adjacent to the bottom of a vertical run.
 - 4. Piping or equipment with damaged and leaking steam tracing is susceptible.
 - 5. Vibrating piping systems have a tendency to inflict damage to insulation jacketing providing a path for water ingress.
 - 6. Insulation jacketing seams located on the top of horizontal piping or improperly lapped or sealed insulation jacketing can lead to CUI.
 - 7. Locations where moisture or trapped water will naturally collect due to gravity drainage before evaporating such as low points in piping runs and insulation support rings on vertical columns, as well as improperly terminated fireproofing.
 - 8. Equipment designed with insulation support rings welded directly to the vessel wall (i.e. with no standoff) can be susceptible, particularly around ladder and platform clips, lifting lugs, nozzles, and stiffener rings.
 - 9. CUI can occur in carbon or low-alloy steel flanges, bolting, and other components under insulation in high-alloy piping systems.
 - 10. Locations where insulation plugs have been removed to permit piping thickness measurements on insulated piping and equipment are a potential source of water ingress.
 - 11. Where piping and equipment have been coated beneath the insulation, localized CUI can still occur where the coating has deteriorated or been damaged.
 - 12. Equipment subjected to long-term or frequent water spray, e.g. from firefighting, fire equipment testing, or supplemental externally applied cooling, is highly susceptible to CUI.
 - 13. 300 series SS equipment insulated with older calcium silicate insulation, which is known to contain high levels of chlorides, can suffer pitting, crevice corrosion, and Cl^- SCC.

3.22.5 Appearance or Morphology of Damage

- a) Carbon steel and low-alloy steels are subject to corrosion having a rough, uneven, somewhat pitted appearance, usually covered with a loose, flaky, non-protective scale attached. The corrosion will be localized to wherever the metal has been kept wet by wet insulation. ([Figure 3-22-1](#) to [Figure 3-22-8](#))
- b) In some cases, the corrosion can appear to be carbuncle-type pitting (usually found under failed coating).
- c) 300 series SS are subject to SCC if chlorides are present. While the duplex stainless steels are less susceptible, SCC failures have occurred in duplex stainless steel due to CUI.

- d) 300 series SS and duplex stainless steel are subject to pitting and crevice corrosion.
- e) Telltale signs of CUI include insulation jacketing damage, bulges or staining of the insulation or jacketing, missing bands, coating damage, or vegetation growing out of the insulation. Bulges may indicate corrosion product buildup.

3.22.6 Prevention/Mitigation

- a) Since most construction materials used in refining are susceptible to CUI damage, mitigation is best achieved by applying an appropriate coating to the equipment prior to insulating.
 - 1. High-quality, immersion-resistant nonmetallic coatings, properly applied to the surfaces to be insulated, can provide long-term protection.
 - 2. Flame-sprayed aluminum coatings have been used on carbon steels. The coating corrodes preferentially by galvanic action, thereby protecting the base metal.
- b) Insulation, insulation jacketing, sealants, and vapor barriers should be properly maintained to prevent moisture ingress.
- c) Thin aluminum foil wrapped on stainless steel piping and equipment beneath the insulation can provide an effective barrier, partly due to the galvanic effect of the aluminum in preventing Cl^- SCC in stainless steel.
- d) Careful selection of insulating materials is important. Both water absorption properties and water retention characteristics are important and should be considered. Some insulating materials absorb little water but still trap water against the pipe or equipment for an extended time because water removal is slow. While closed-cell foam glass materials will hold less water and, therefore, might be less prone to causing CUI, studies show that an open cell structure provides a path for water vapor to escape faster, allowing the insulation to dry quicker. Faster drying time, corresponding to less metal wetting time, should help mitigate CUI.
 - 1. Types of open cell insulation that limit and delay water ingress have been developed.
 - 2. Water absorption and retention properties of insulation materials can be tested per EN 13472 or ASTM C1134.
- e) Insulation with added corrosion inhibitor is available.
- f) Low-chloride insulation should be used on 300 series SS to minimize the potential for pitting and Cl^- SCC.
 - 1. Some manufacturers supply insulation certified to be low chloride. Thermal insulation materials can be tested per ASTM C871 to evaluate chloride content and/or ensure it satisfies a specified limit.
- g) Insulation plugs removed for UT thickness measurements should be promptly replaced and sealed. Several types of removable plugs that permit inspection and identification of inspection points are commercially available.
- h) Consider available alternatives in order to avoid the use of insulation where practical.
 - 1. Personnel protection from hot piping can be provided using metal-cage-type standoffs rather than insulation.
 - 2. It is not usually possible to modify operating conditions; however, consideration should be given to removing the insulation on equipment where heat conservation is not as important.

3.22.7 Inspection and Monitoring

- a) An inspection plan for CUI should be a structured, systematic approach starting with prediction and analysis per the CUI planning information contained in API 510, API 570, and API 583. [API 583 was created specifically for CUI/CUF (corrosion under fireproofing) and should be referenced for a deeper understanding of inspection for these damage mechanisms.] The inspection plan should consider:

1. history of CUI leaks,
 2. operating temperatures that may give rise to CUI,
 3. type and age/condition of coating, and
 4. type, age, and condition of the insulation material.
- b) Additionally, an external VT of the equipment, looking for evidence of insulation system damage, mastic and/or sealant damage, signs of water penetration, rust in gravity drain areas on equipment and piping, and signs of process fluid leaks, will help prioritize the effort.
- c) Although external insulation may appear to be in good condition, CUI damage may still be occurring in isolated areas not thought to be susceptible. The owner/user generally determines the extent of CUI inspection, including the extent of insulation removal for inspection, based on inspection and CUI history and other factors as described above.
1. An effective way to find all CUI damage is complete removal of insulation and inspection for damage using VT, UT, and/or a pit gage, as applicable, for determining remaining thickness, or PT to examine for external Cl^- SCC of austenitic stainless steels.
 2. Inspection by RT (density and/or profile) or UT thickness inspection (e.g. using high-resolution pigging) can also provide a high level of CUI detection confidence, depending on the extent of inspection, i.e. the percent of potentially affected piping inspected.
 3. In some instances, insulation “windowing” can be used to remove insulation in selected areas thought to be more susceptible to CUI damage than others and inspecting for damage using VT, UT, and/or a pit gage, as applicable, for determining remaining thickness, or PT to examine for external Cl^- SCC of austenitic stainless steels. However, this may be less effective than complete insulation removal.
- d) Non-invasive, commercially available methods can be used to identify either wet insulation or CUI damage under the insulation without removing the insulation; however, these methods should not be expected to find 100 % of the damage. Each of these methods is discussed in API 583, including advantages and disadvantages of each. Most are screening techniques that may help identify where there is a higher probability of CUI damage and where insulation stripping may be needed to further assess and quantify the damage. These methods include, but may not be limited to:
1. GWT;
 2. RT (including profile, density, flash, radiometric profiling, real-time, computed, and digital);
 3. PEC;
 4. neutron backscatter (for identifying wet insulation); and
 5. infrared thermography imaging (for identifying wet insulation).
- e) Common areas of higher CUI concern in process units are high-moisture areas such as those down-wind from cooling towers (the drift zone), near steam vents, under deluge systems, exposed to acid vapors, or near supplemental cooling with water spray.

3.22.8 Related Mechanisms

Atmospheric corrosion (3.8), oxidation (3.48), oxygenated water corrosion (3.49), concentration cell corrosion (3.19), and Cl^- SCC (3.17).

3.22.9 References

1. API Recommended Practice 583, Corrosion Under Insulation and Fireproofing, American Petroleum Institute, Washington, DC.

2. API Recommended Practice 581, *Risk-Based Inspection Methodology*, American Petroleum Institute, Washington, DC.
3. NACE Standard SP0198, *Control of Corrosion Under Thermal Insulation and Fireproofing Materials—A Systems Approach*, NACE International, Houston, TX.
4. W.I. Pollock and C.N. Steely, *Corrosion Under Wet Thermal Insulation*, NACE International, Houston, TX, 1990.
5. M.M. Chauviere et al., “Managing CUI in Aging Refinery Pressure Vessels,” Paper No. 07566, *Corrosion/2007*, NACE International, Houston, TX.
6. API 510, *Pressure Vessel Inspection Code: In-Service Inspection, Rating, Repair, and Alteration*, American Petroleum Institute, Washington, DC.
7. API 570, *Piping Inspection Code: In-service Inspection, Repair, and Alteration of Piping Systems*, American Petroleum Institute, Washington, DC.
8. A.C. Haaland, “Designing against CUI—What Are the Implications of the Test Method Chosen?” Paper No. RISK16-8742, *Corrosion Risk Management Conference*, NACE International, Houston, TX, May 2016.
9. C. Zwaag and S.N. Rasmussen, “Cyclic CUI Testing of Insulation Materials,” Paper No. 8877, *Corrosion/2017*, NACE International, Houston, TX.
10. EN 13472, *Thermal Insulating Products for Building Equipment and Industrial Installations—Determination of Short Term Water Absorption by Partial Immersion of Preformed Pipe Insulation*, Available as CSN EN 13472, DIN EN 13472, and BS 13472, European Committee for Standardization, Brussels, Belgium.



Figure 3-22-1—Piping tee in a 1000 psig ethylene line before insulation removal.



Figure 3-22-2—Close-up of the tee in Figure 3-21-1 after insulation removal.



Figure 3-22-3—CUI of a 30-in. carbon steel butadiene line showing highly localized corrosion that could only be found by stripping the entire line. Note the 0.25-in. (6.5-mm) diameter hole at arrow.



Figure 3-22-4—CUI of a nozzle on the bottom head of a pressure vessel.



Figure 3-22-5—CUI of a nozzle on the top head of a pressure vessel.

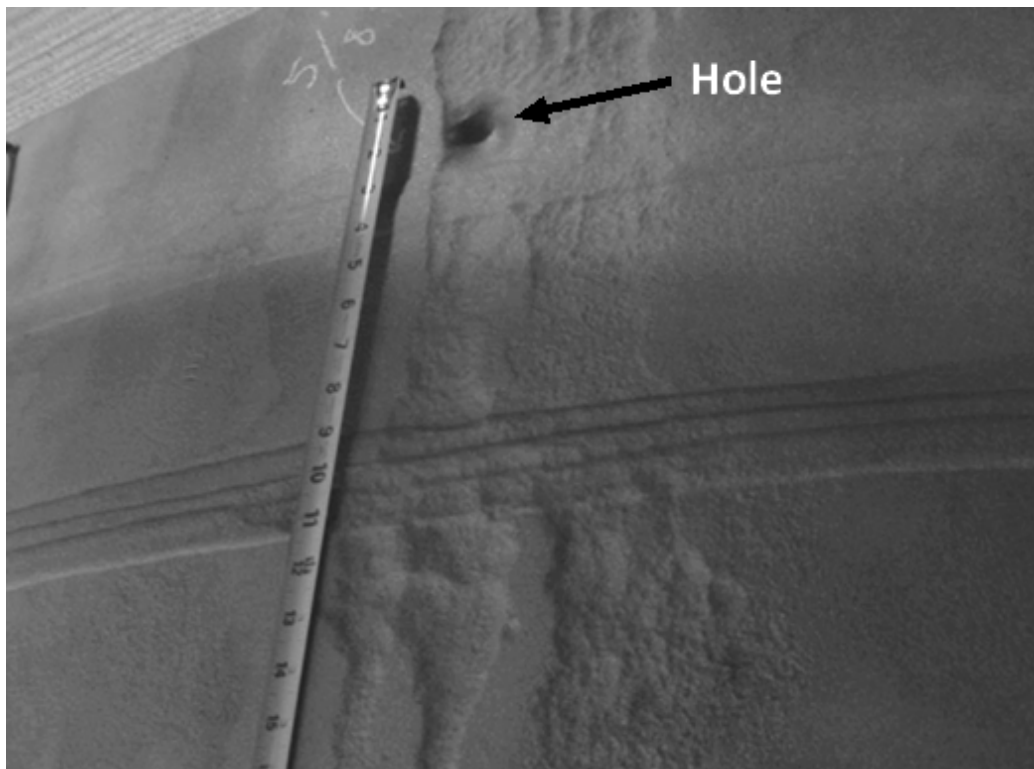


Figure 3-22-6—CUI of a vessel wall. Note the leak at the arrow.



Figure 3-22-7—CUI at attachment supports and on the vessel head.



Figure 3-22-8—CUI of a carbon steel level bridge.

3.23 Creep and Stress Rupture

3.23.1 Description of Damage

- a) At high temperatures [typically greater than half the absolute melting temperature in °R (°K)], metal components can continuously deform under load, even below their elastic yield stress. This time-dependent deformation of stressed components is known as creep.
- b) Exposure to stress at high temperatures initially promotes void formation at grain boundary triple points, which with time grow to form fissures and, later, cracks.
- c) As fissures and cracks coalesce, failure can occur, although the gross deformation associated with tensile overloading is not observed.

3.23.2 Affected Materials

All metals and alloys.

3.23.3 Critical Factors

- a) The rate of creep deformation (creep rate or strain rate) is a function of the material, applied stress, and temperature.
 1. Creep rate is very sensitive to relatively small changes in temperature or stress. Generally, a temperature increase of about 25 °F (15 °C) or a 15 % increase in stress can cut the remaining life in half, or worse, depending on the alloy.
- b) [Table 3-23-1](#) lists threshold temperatures for different metals above which creep damage is a concern. If the metal temperature exceeds these values, creep deformation and creep cracking can eventually occur.
- c) The creep life of metal components becomes extremely long at temperatures below their threshold in [Table 3-23-1](#), even at the high stresses near a crack tip.
- d) Creep deformation is the result of relative movement between individual (microscopic size) grains or other discontinuities within the metal. As creep progresses and cracks develop and grow from microscopic size to macroscopic size, the cracks eventually grow through the wall resulting in failure, at which point they are clearly visible.
 1. Because a coarse-grained material has less grain boundary surface area than a fine-grained material, a material heat treated to have a coarse-grained structure will generally have better creep strength than the same material with a fine-grained structure.
- e) Creep cracking, once initiated, can progress rapidly.
- f) Increased stress due to loss in thickness from corrosion will reduce time to creep failure.
- g) The appearance of creep cracking with little or no apparent deformation usually indicates that the material has low creep ductility. Low creep ductility is:
 1. more pronounced in higher tensile strength materials and welds,
 2. more prevalent at lower temperatures in the creep range or with low stresses at the upper temperatures in the creep range,
 3. more likely in a coarse-grained material than in a fine-grained material,
 4. not evidenced by a deterioration of ambient temperature properties, and
 5. promoted by certain carbide types in some Cr-Mo steels.

3.23.4 Affected Units or Equipment

- a) Creep damage is found in high-temperature equipment operating in the creep temperature range. Heater tubes in fired heaters, as well as tube supports, hangers, and other furnace internals, as well as high-pressure steam tubes in boilers, can be susceptible to creep.
- b) Hot-wall catalytic reforming reactors, reactor piping, furnace tubes, hydrogen-reforming furnace tubes, hot-wall FCC reactors, and FCC main fractionator and regenerator internals all operate in or near the creep temperature range.
- c) Low creep ductility failures have occurred in weld HAZs at nozzles and other high-stress areas in $1\frac{1}{4}\text{Cr}-\frac{1}{2}\text{Mo}$ catalytic reformer reactors. Cracking has also been found at long seam welds in some high-temperature $1\frac{1}{4}\text{Cr}-\frac{1}{2}\text{Mo}$ piping and reactors in catalytic reformers, primarily due to “peaking” of the long-seam welds.
- d) Welds joining dissimilar materials (e.g. ferritic to austenitic welds) may suffer creep-related damage at high temperatures due to differential thermal expansion stresses.

3.23.5 Appearance or Morphology of Damage

- a) The initial stages of creep damage can only be identified by scanning electron microscope (SEM) metallography. Creep voids typically show up at the grain boundaries. At later stages, they grow into microfissures and then cracks. When the fissures run the entire length of a grain boundary, they can be seen by standard optical microscope metallography, although they will not necessarily be easy to find.
- b) At temperatures well above the threshold limit, noticeable deformation may be observed. For example, heater tubes may suffer long-term creep damage and exhibit significant, measurable bulging before rupture occurs. The amount of deformation before fracture is highly dependent on the material and the combination of temperature and stress level. ([Figure 3-23-1](#) to [Figure 3-23-3](#))
- c) In vessels and piping, creep cracking can occur where high metal temperatures and stress concentrations occur together, such as near major structural discontinuities including pipe tee joints and vessel nozzles, as well as at weld flaws.

3.23.6 Prevention/Mitigation

- a) There is little that inspectors or operators can do to prevent this damage once a susceptible material has been placed into creep service, other than to minimize the metal temperature, particularly with fired heater tubes. Avoiding stress concentrations is important during design and fabrication.
- b) Low creep ductility can be minimized by the careful selection and specification of materials. See SRC ([3.54](#)).
- c) Creep damage is not reversible. Once damage or cracking is able to be detected, much of the life of the component has been used up, and typically the options are to repair or replace the damaged component. Higher PWHT in some cases can produce a more creep ductile material with longer life.
 - 1. Equipment—Repair of creep damaged catalytic reformer reactor nozzles has been successfully accomplished by grinding out the affected area (making sure all the damaged metal is removed), re-welding, and careful blend grinding to help minimize stress concentration. PWHT temperatures must be carefully selected and may require a higher PWHT than originally specified.
 - 2. Fired Heater Tubes—Alloys with improved creep resistance may be required for longer life. Heaters should be designed and operated to minimize hot spots and localized overheating, e.g. due to flame impingement or improper burner operation. ([Figure 3-23-3](#)) Minimizing process-side fouling and deposits and fire-side deposits and scaling, both of which can necessitate overfiring to maintain process temperatures, can maximize tube life.
 - 3. Remaining life of heater tubes can be assessed in accordance with API 579-1/ASME FFS-1.

4. Retirement criteria based on diametric growth and loss of wall thickness are highly dependent on the tube material and the specific operating conditions. Different retirement strategies may be needed for different situations.

3.23.7 Inspection and Monitoring

- a) Creep deformation and the associated microvoid formation, fissuring, and dimensional change are not effectively found by any one inspection technique. A combination of proper NDE techniques (surface and volumetric), dimensional measurements, and field metallographic replication (FMR) are often needed. Destructive sampling and metallographic examination are generally used to confirm damage.

1. Conventional NDT methods, e.g. WFMT, VT, PT, or UT techniques, are not able to detect creep damage prior to the formation of a creep crack.
2. FMR is typically used where evidence has been found through other inspection methods.

NOTE FMR performed on the surface of a component will not show subsurface damage and will miss internal creep fissuring.

- b) For pressure vessels, inspection is generally focused on welds of Cr-Mo alloys operating in the creep range. The choice of NDE methods may depend on the severity of any apparent damage. On the viewable surface, VT is generally performed, followed up with PT or WFMT. For subsurface examination for cracking or gross fissuring, angle beam UT (SWUT or PAUT) or other high-resolution NDE methods, such as TOFD, can also be employed, although the early stages of creep damage are very difficult to detect.

- c) Fired heater tubes are typically inspected for evidence of overheating, bulging, corrosion, and erosion as follows.

1. Tubes can be VT examined for bulging, blistering, cracking, sagging, bowing, or rubbing wear. VT will not detect internal creep damage but is used to identify areas where further NDE may be needed.
2. UT wall thickness measurements of selected heater tubes can be made where wall losses are most likely to occur. UT thickness measurements will not detect creep damage but are used for creep examination to identify areas where further NDE may be needed.
3. Tubes can be examined for evidence of diametric growth due to creep with a strap or go/no go gauge. Dimensional inspection will not detect internal creep damage but will detect large, apparent creep deformation and also identify areas where further NDE may be needed.
4. In-line inspection (smart pigging) of heater tubes will provide a more complete assessment of remaining wall thickness and diameter growth. However, it is unlikely to detect internal creep damage, and further NDE may be needed.
5. Automated inspection devices (crawlers) are commercially available for inspecting hydrogen reformer heater tubes. The selection of such equipment for inspection, as well as analysis and interpretation of results, involves careful evaluation.

3.23.8 Related Mechanisms

Short-term overheating—stress rupture (3.55), SRC (3.54), and dissimilar metal weld (DMW) cracking (3.26).

3.23.9 References

1. API 579-1/ASME FFS-1, *Fitness-For-Service*, American Petroleum Institute, Washington, DC.
2. API Standard 530, *Calculation of Heater-tube Thickness in Petroleum Refineries*, American Petroleum Institute, Washington, DC.
3. API Standard 660, *Shell-and-Tube Heat Exchangers*, American Petroleum Institute, Washington, DC.

Table 3-23-1—Threshold Temperatures for Creep (Reference 1)

Material	Temperature Limit
Carbon steel [UTS > 414 MPa (60 ksi)]	650 °F (345 °C)
Carbon steel [UTS > 414 MPa (60 ksi)]	700 °F (370 °C)
Carbon steel—Graphitized	700 °F (370 °C)
C-½Mo	750 °F (400 °C)
1¼Cr-½Mo—Normalized and tempered	800 °F (425 °C)
1¼Cr-½Mo—Annealed	800 °F (425 °C)
2¼Cr-1Mo—Normalized and tempered	800 °F (425 °C)
2¼Cr-1Mo—Annealed	800 °F (425 °C)
2¼Cr-1Mo—Quenched and tempered	800 °F (425 °C)
2¼Cr-1Mo-V	825 °F (440 °C)
3Cr-1Mo-V	825 °F (440 °C)
5Cr-½Mo	800 °F (425 °C)
7Cr-½Mo	800 °F (425 °C)
9Cr-1Mo	800 °F (425 °C)
9Cr-1Mo-V	850 °F (455 °C)
12 Cr	900 °F (480 °C)
AISI Type 304 and 304H	950 °F (510 °C)
AISI Type 316 and 316H	1000 °F (540 °C)
AISI Type 321	1000 °F (540 °C)
AISI Type 321H	1000 °F (540 °C)
AISI Type 347	1000 °F (540 °C)
AISI Type 347H	1000 °F (540 °C)
Alloy 800	1050 °F (565 °C)
Alloy 800H	1050 °F (565 °C)
Alloy 800HT	1050 °F (565 °C)
HK-40	1200 °F (650 °C)



Figure 3-23-1—A pinched Alloy 800H pigtail with opened-up creep fissures on the surface.

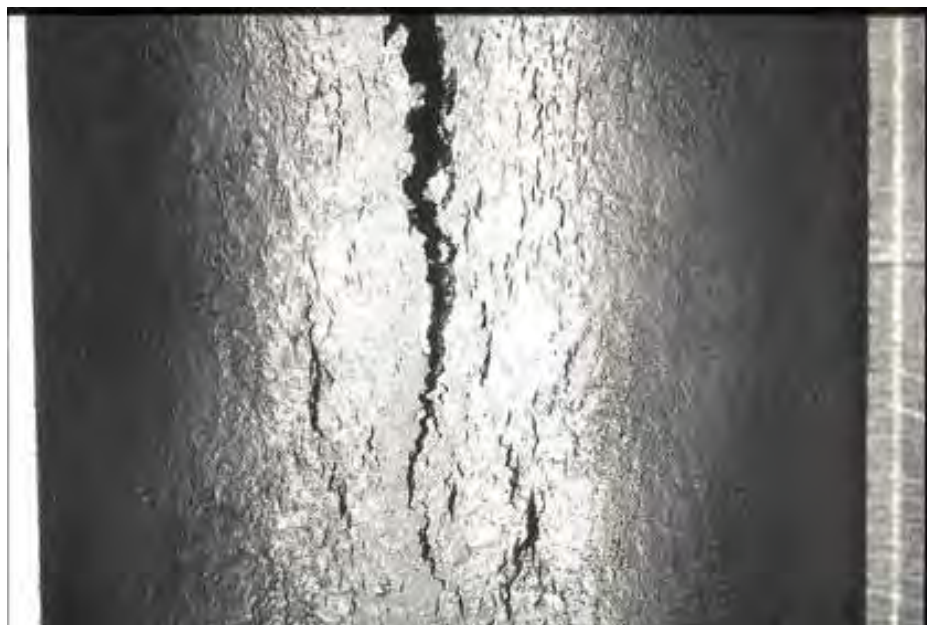


Figure 3-23-2—Creep rupture of an HK40 heater tube.



(a)



(b)

Figure 3-23-3—Creep failure of Type 310 SS heater tube guide bolt after approximately 7 years of service at 1400 °F (760 °C). (a) Cross section at 10X magnification, as-polished. (b) Voids and intergranular separation characteristic of long-term creep (magnification 100X, etched).

3.24 Dealloying [See Graphitic Corrosion (3.33) for Dealloying of Cast Iron]

3.24.1 Description of Damage

- a) Dealloying is the result of what appears to be a selective corrosion mechanism in which one or more constituents of an alloy are preferentially attacked, leaving a lower-density (dealloyed), often porous structure.
- b) Component failure may occur suddenly and unexpectedly because mechanical properties of the dealloyed material are significantly degraded.

3.24.2 Affected Materials

Primarily copper alloys (brasses and bronzes and Cu-Ni alloys) as well as Alloy 400.

3.24.3 Critical Factors

- a) Factors that influence dealloying include the composition of the alloy and the exposure conditions including temperature, presence or increase levels of oxygen or aeration, pH, and exposure time.
- b) Dealloying occurs with several different alloys but is usually limited to very specific alloy-environment combinations.
- c) Exact conditions under which dealloying occurs are often hard to define and damage may occur progressively over many years in service.
- d) Stagnant or low-flow conditions can promote dealloying.
- e) Common examples of where dealloying has been found to occur are listed in [Table 3-24-1](#).

3.24.4 Affected Units or Equipment

- a) Copper alloys in cooling water applications, including tubes and tubesheets, can be susceptible to dealloying in some brackish and seawater applications. Dealloying can also occur in some freshwater or domestic water systems.
- b) In BFW piping systems and after-boiler systems, bronze pumps, Alloy 400 strainers, brass pressure gage fittings, steam turbine surface condenser tubes, and the like may suffer dealloying.
- c) Alloy 400 exposed to HF acid in HF alkylation plants can be susceptible to denickelification, particularly above 300 °F (50 °C) or if oxygen is present.

3.24.5 Appearance or Morphology of Damage

- a) There is often a significant color change, with the affected area becoming the color representative of the remaining material. The surface of the affected area can also have a dull or deeply etched (corroded) appearance as one element is removed from the alloy. However, depending on the alloy, the outward appearance of the affected material may not be noticeable upon VT, even where the full wall thickness is degraded.
- b) Attack may be uniform through the cross section (layer-type) ([Figure 3-24-1](#)), or it can be localized (plug-type) ([Figure 3-24-2](#)).
- c) In some cases, the original material is completely dealloyed, yet the component exhibits virtually no dimensional or other visible changes.
- d) The porous, dealloyed material is often brittle and weak and may be easily broken off, even by hand. Thru-wall dealloying can result in fracture of the component or holes.

3.24.6 Prevention/Mitigation

- a) It is often difficult to predict whether conditions will be conducive to dealloying in a particular environment or service, so one must be cognizant of the susceptibility of certain alloys and the possible resulting consequences.
- b) Select “inhibited” versions of copper alloys. In some cases, resistance to dealloying can be improved by the addition of certain alloying elements, so that an alloy with only a slightly modified composition may be resistant. For example, admiralty brass is inhibited by the addition of a very small amount of phosphorous, antimony, or arsenic, while tin inhibits dealloying of other copper alloys. It is now typical for brass and bronze components used in refining applications to be sold only with the inhibited chemistry
- c) Dealuminification of aluminum-bronze can be prevented by heat treatment to produce an α and β microstructure.
- d) Use alternative materials that are not susceptible to dealloying in the environment(s) to which they will be exposed.
- e) Continued degradation of a dealloyed component can only be prevented by altering the exposure conditions or replacing it with a resistant material.
- f) Depending on the alloy-environment combination, cathodic protection or barrier coatings may be effective.
- g) Prevent the entry of oxygen into HF acid alkylation units.

3.24.7 Inspection and Monitoring

- a) Many alloys change color in the affected area; however, scale removal may be required to determine the depth of attack.
- b) Dealloying in brasses is visually evident by a reddish, copper color instead of the yellow brass color.
- c) Metallographic examination may be required to confirm the extent of damage.
- d) A significant reduction in hardness may accompany dealloying, although affected areas may be localized.
- e) Acoustic techniques (loss of “metallic ring”) and ultrasonic attenuation are applicable, but UT thickness measurements are not.
- f) FFS analysis of dealloyed components should consider that the dealloyed portion may be brittle and contribute little or no mechanical strength or load-bearing capability.
- g) Electromagnetic techniques may be used to screen for dealloying. It is critical that the appropriate calibration standards be used. ECT can screen for dealloying in brass.

3.24.8 Related Mechanisms

Graphitic corrosion of cast irons (3.33). Dealloying is often referred to by the element removed, as in dezincification, destannification (tin), denickelification, and dealuminification. Dealloying has also been referred to as selective leaching.

3.24.9 References

1. *ASM Handbook—Corrosion*, Volume 13, ASM International, Materials Park, OH.
2. A. Cohen, "Copper and Copper-base Alloys," *Process Industries Corrosion—The Theory and Practice*, NACE International, Houston, TX, 1986, pp. 479–501.
3. R.D. Port and H.M. Herro, *The Nalco Guide to Boiler Failure Analysis*, McGraw-Hill, New York, NY, 1991, pp. 259–263.
4. *ASM Handbook—Failure Analysis and Prevention*, Volume 11, ASM International, Materials Park, OH.

Table 3-24-1—Combinations of Alloys and Environment Subject to Dealloying (Reference 1)

Alloy	Environment	Element Removed
Brasses (>15 % Zn) *	Many waters, especially stagnant conditions	Zinc (dezincification)
Aluminum bronze (primarily with > 8 % Al)	HF acid, acids w/chloride ions, seawater	Aluminum (dealuminification)
Silicon bronzes	High-temperature steam and acidic species	Silicon (desiliconification)
Tin bronzes	Hot brine or steam	Tin (destannification)
Copper nickels (70 to 30)	High heat flux and low water velocity	Nickel (denickelification)
Monel	Hydrofluoric and other acids	Nickel (denickelification)

* The extent of dezincification increases with increasing zinc content.

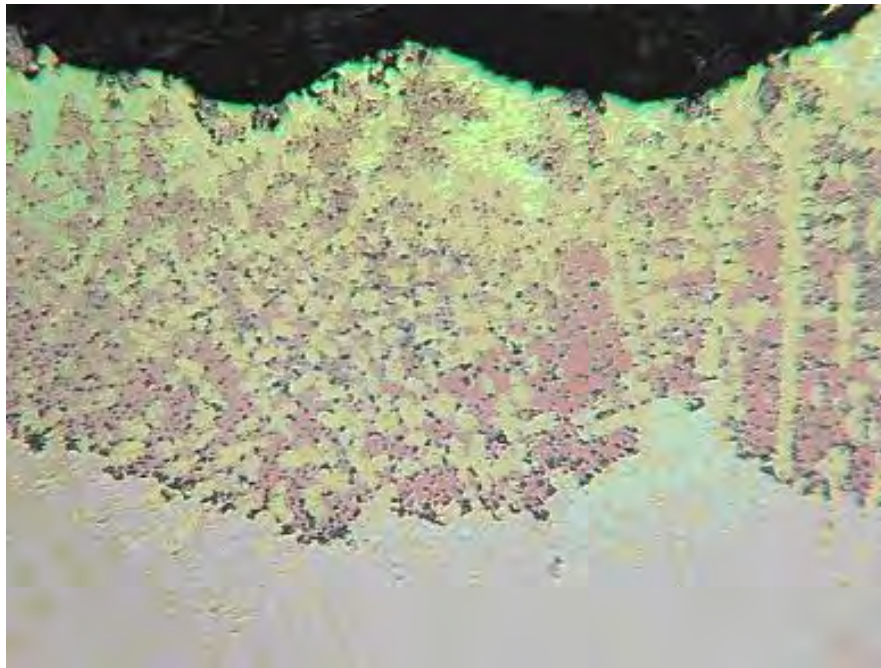


Figure 3-24-1—Cross section of a silicon-brass alloy, C87500, pump impeller from stagnant fire-water service. Layer-type dezincification depleted the zinc and left this porous red color of the copper. Magnification 50X.



Figure 3-24-2—A zone of denickelification in an Alloy 400 valve plug (at the port), due to oxygen contamination in hot hydrofluoric acid.

3.25 Decarburization

3.25.1 Description of Damage

A condition where a steel loses strength due to the removal of carbon and carbides leaving only an iron matrix. Decarburization occurs during exposure to high temperatures, during heat treatment, from exposure to fires, or from high-temperature service in a gaseous environment. Loss in room-temperature tensile strength and creep strength may potentially occur.

3.25.2 Affected Materials

Carbon steels and low-alloy steels.

3.25.3 Critical Factors

- a) Time, temperature, and carbon activity of the process stream are the critical factors.
- b) The material must be exposed to a gas phase that has a low carbon activity so that carbon in the steel will diffuse to the surface to react with gas phase constituents.
- c) The extent and depth of decarburization is a function of the temperature and exposure time.
- d) Shallow decarburization can slightly decrease the strength of the material but typically has no detrimental effect on the overall performance of the component. However, it is indicative that the steel may have been overheated and suggests other effects may be present [e.g. decarburization associated with high-temperature hydrogen attack (HTHA) in hydrogen services].

3.25.4 Affected Units or Equipment

- a) Decarburization can occur in almost any equipment that has been heat treated, exposed to elevated service temperatures, or exposed to a fire.
- b) Piping and equipment in hot hydrogen service in hydroprocessing units or catalytic reforming units, as well as most fired heater tubes, can be decarburized in service. Pressure vessel components that are hot formed during fabrication can be affected.

3.25.5 Appearance or Morphology of Damage

- a) Damage can be verified by metallography.
- b) Damage occurs on the surface exposed to the gas environment but in extreme cases may be through the wall.
- c) The decarburized layer will be free of carbide phases. Carbon steel will become pure iron. ([Figure 3-25-1](#) and [Figure 3-25-2](#))

3.25.6 Prevention/Mitigation

- a) Decarburization can be controlled by controlling the chemistry of the gas phase and alloy selection.
- b) Alloy steels with chromium and molybdenum form more stable carbides and are more resistant to decarburization.
- c) Steels operating in high-temperature hydrogen environments should be selected in accordance with API RP 941.

3.25.7 Inspection and Monitoring

- a) VT is ineffective for detecting decarburization.
- b) Inspection for decarburization in the initial stages of attack is difficult (and generally unnecessary).
- c) FMR can be applied if the process-side surfaces are accessible, but it is often inconclusive.
- d) Decarburization results in a softening that can be confirmed by hardness testing if the depth of decarburization is sufficient to enable accurate hardness testing results. This should be considered a screening tool. If the surface hardness falls below a set limit, which would differ between materials, then further testing (e.g. sampling and metallography) would likely be needed.
- e) Decarburization can only be determined accurately by a chemical or physical test, which typically requires destructive sampling. Sampling location, condition, and preparation are critical.

3.25.8 Related Mechanisms

HTHA (3.36).

3.25.9 References

1. *ASM Handbook—Corrosion*, Volume 13, ASM International, Materials Park, OH.
2. API Recommended Practice 573, *Inspection of Fired Boilers and Heaters*, American Petroleum Institute, Washington, DC.
3. API Recommended Practice 941, *Steels for Hydrogen Service at Elevated Temperatures and Pressures in Petroleum Refineries and Petrochemical Plants*, American Petroleum Institute, Washington, DC.
4. G. Vander Voort, "Understanding and Measuring Decarburization," *Advanced Materials & Processes*, February 2015, pp. 22–27.
5. G. Vander Voort, "Decarburization," Vac Aero International, <http://vacaero.com/information-resources/metallography-with-george-vander-voort/1342-decarburization.html>.
6. L. Garverick, *Corrosion in the Petrochemical Industry*, Second Edition, pp. 29, 150, 154, 227, 321, and 387, ASM International, Materials Park, OH.

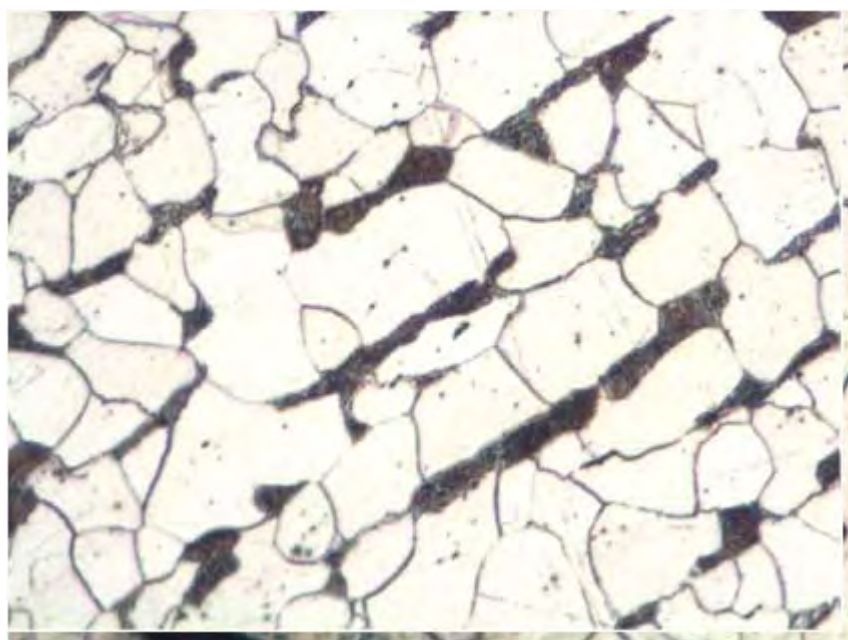


Figure 3-25-1—Typical low-carbon-steel microstructure showing ferrite phase (light grains) and pearlite (dark layered constituent).

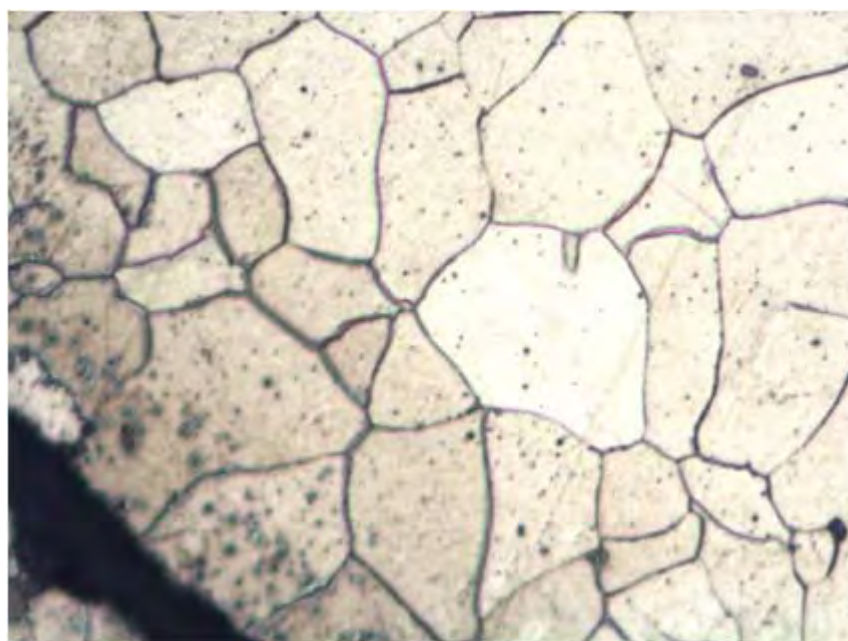


Figure 3-25-2—Microstructure illustrating a decarburized low carbon steel where the strength-providing pearlite constituent has been decomposed as the result of the removal of carbon atoms by diffusion to the surface.

3.26 Dissimilar Metal Weld Cracking

3.26.1 Description of Damage

There are four situations that can result in the cracking of DMWs. In one, operation at elevated temperature, about 500 °F (260 °C) or higher, results in high differential thermal expansion stresses at the weld that lead to creep cracking or creep-fatigue cracking. In the second, operation in a wet H₂S or similarly severe hydrogen charging environment leads to cracking in the hard, dissimilar metal mixed zone in the weld created when the two metals are melted together. The third, with some similarities to the second, occurs on the carbon steel side in welds between carbon steel and Alloy 400 in hydrofluoric acid service due to HE and/or fluoride wedging. In the fourth situation, DMW joints in (and weld overlay on) equipment in high-temperature hydrogen service can suffer disbonding between the two metals. This is commonly referred to as hydrogen disbonding. All four cases typically involve carbon steel or low-alloy steel welded to an austenitic (300 series) stainless steel or a nickel-based alloy.

3.26.2 Affected Materials

The most common are ferritic materials such as carbon steel and low-alloy steels welded to austenitic stainless steels. In HF acid service, it involves carbon steel welded to Alloy 400. Cracking due to high differential thermal expansion stress can occur in any material combination having widely differing thermal expansion coefficients.

3.26.3 Critical Factors

a) Thermal expansion related cracking. (See [Figure 3-26-1](#) and [Figure 3-26-2](#).)

1. Important factors include the type of filler metal used to join the materials, heating and cooling rate, metal temperature, time at temperature, weld geometry, and frequency of thermal cycling.
2. Cracking can occur because the coefficients of thermal expansion of ferritic materials (e.g. steels) and austenitic materials (e.g. 300 series SS and nickel-based alloys) differ by about 25 % to 30 %. (See [Table 3-26-1](#).) At high operating temperatures, the differences in thermal expansion lead to high shear stresses concentrated at the fusion line, primarily in the ferritic-side HAZ. The higher the operating temperature, the greater the stress created by the differential thermal expansion between the metals. Ferritic/austenitic joints can generate significant thermal expansion/thermal fatigue stresses at temperatures greater than 500 °F (260 °C). Cracking is most common at service temperatures greater than 800 °F (425 °C).
3. Thermal cycling aggravates the problem. Stresses during start-up and shutdown can be significant.
4. Stresses acting on the weldment are significantly higher when an austenitic stainless steel filler metal is used. A nickel-based filler metal has a coefficient of thermal expansion that is closer to carbon steel, resulting in significantly lower stress at elevated temperatures.
5. The problem is aggravated by the diffusion of carbon out of the HAZ of the ferritic material and into the austenitic weld metal where it is more soluble. The loss of carbon creates a “soft zone” with reduced creep strength in the ferritic material HAZ, thereby increasing the cracking probability. ([Figure 3-26-3](#)) The temperature at which carbon diffusion becomes a concern is above 800 °F (425 °C) for carbon steel and above 950 °F (510 °C) for low-alloy steels.
6. Poor geometry of the weld, excessive undercut, and other stress intensification factors will promote crack formation.
7. In environments that promote liquid ash corrosion, weld cracking problems may be accelerated by stress-assisted corrosion. The ferritic HAZ will preferentially corrode due to the large thermal strain. The results are long, narrow, oxide wedges that parallel the fusion line of the weld. ([Figure 3-26-10](#))

b) Hard mixed metal zone related cracking.

1. DMWs between ferritic and austenitic materials that are made with a 300 series SS or nickel-based filler metal result in a narrow region (mixed zone) of high hardness along the fusion line on the ferritic steel side. These high-hardness zones render the material susceptible to HE types of environmental cracking such as SSC or hydrogen stress cracking. (Figure 3-26-4 and Figure 3-26-5) PWHT of the weldment will not prevent environmental cracking if the weld is exposed to wet H₂S conditions.
2. Poor geometry of the weld, excessive undercut, and other stress intensification factors will promote crack formation.

c) Cracking in HF acid.

1. Locating a CS to Alloy 400 weld in locations exposed to hydrofluoric acid (anhydrous HF, water containing HF, and dilute HF) creates a corrosive galvanic cell. The corrosion reaction produces hydrogen on the metal surface, which can then diffuse into the weldment. The problem is enhanced by high hardness in the coarse-grained HAZ of the carbon steel.

d) Hydrogen disbanding.

1. Joint design is critical for DMWs in high-temperature service in hydrogen environments. The weld joints must be carefully designed and inspected to prevent hydrogen disbanding. (Figure 3-26-6 to Figure 3-26-9)

3.26.4 Affected Units or Equipment

a) DMWs are utilized in special applications in refineries and other process plants. Examples of DMWs include the following.

1. Welds used to join clad pipe in locations such as transitions in hydroprocessing reactor outlet piping from overlaid low-alloy Cr-Mo nozzles or piping to solid 300 series SS pipe.
2. Hydroprocessing exchanger inlet and outlet piping.
3. Alloy transitions inside fired heaters (e.g. 9Cr to 317L in a crude furnace).
4. Hydrogen reformer furnace 1.25Cr inlet pigtails to Alloy 800 sockolets or weldolets on hydrogen reformer tubes.
5. Hydrogen reformer furnace Alloy 800 outlet cones to CS or 1.25Cr refractory lined transfer lines.
6. Welds joining clad pipe sections to themselves or to unclad carbon or low-alloy steel pipe (e.g. Alloy C276 clad CS piping in crude unit overhead system).
7. Nickel-based alloy welds joining socket weld valves in 5 and 9 Cr piping systems.
8. Carbon steel to Alloy 400 welds in HF alkylation units.
9. 300 series SS weld overlay in numerous refinery reactors and pressure vessels.
10. Similar DMWs have been used in FCC unit reactors and regenerator vessels and in coker units.

b) All superheaters and reheaters that have welds between ferritic materials (1.25Cr-0.5Mo and 2.25Cr-1Mo) and austenitic materials (300 series SS including 304H, 321H, and 347H).

3.26.5 Appearance or Morphology of Damage

- a) In most cases, differential thermal expansion cracks form at the toe of the weld in the HAZ of the ferritic material. (Figure 3-26-4 to Figure 3-26-10) Welds joining pipes or tubes are the most common problem area, but support lugs or attachments of cast or wrought 300 series SS to 400 series SS are also affected.
- b) Hard mixed zone cracking occurs along the fusion line, through the mixed zone identifiable by metallographic examination.
- c) Carbon steel to Alloy 400 weld damage in HF will be characterized by localized corrosion of the carbon steel HAZ area and hydrogen stress cracking along the fusion line or coarse-grained portion of the HAZ. (Figure 3-26-11 and Figure 3-26-12)
- d) Hydrogen disbonding cracks form at the interface between the austenitic weld metal and the ferritic base metal.

3.26.6 Prevention/Mitigation

- a) For high-temperature applications, nickel-based filler metals that have a coefficient of thermal expansion closer to carbon and low-alloy steels may dramatically increase the life of the joint, because of the significant reduction in thermal stress acting on the steel (ferritic) side of the joint. Refer to API 577 and API 582 for additional information on filler metal selection, welding procedures, and weld inspection.
- b) For high-temperature installations, consider installing a pup piece that has an intermediate thermal expansion coefficient between the two materials to be joined.
- c) Use of a shallower weld prep bevel or a compound angle bevel increases the effective weld length and alters the stress field, which may promote longer life.
- d) If 300 series SS welding electrodes are used, the DMW should be placed in a low-temperature region.
- e) In steam-generating equipment, the weld at the high-temperature end should be made in the penthouse or header enclosure, out of the heat transfer zone.
- f) For high-temperature service, consider buttering the ferritic side of the joint with the stainless steel or nickel-based filler metal and perform PWHT prior to completing the DMW. PWHT will reduce residual stress at the ferritic-austenitic interface and thereby reduce the likelihood of high-temperature DMW cracking.
- g) On buttered joints, the thickness of the weld metal should be a minimum of 0.25 in. (6 mm) after the bevel is machined, in order to avoid creating an HAZ in the base metal beneath the butter layer when the attachment weld is made.
- h) Avoid using DMWs for socket welds or pressure-retaining fillet welds at temperatures above 250 °F.
- i) Avoid using DMWs in wet H₂S services. Where unavoidable, specially designed weld configurations may be needed to avoid the potentially hard HAZ from contacting the environment or to avoid the formation of a thru-wall hard HAZ, e.g. by alloy-overlaying the base metal for some distance beyond the alloy weld joint.
- j) Avoid using DMWs in HF acid service. Where necessary, locate the carbon steel to Alloy 400 transition where the exposure to free HF is minimal. In piping, use flanged connections. In lined columns, locate the DMW in an acid-free zone. Where exposure to HF cannot be avoided, take precautions to avoid high-hardness HAZs in carbon steel, particularly in older, pre-1980 steels. See NACE SP0472.

3.26.7 Inspection and Monitoring

Inspection of complex, multi-material welded joints may require consulting a subject matter expert and is beyond

the scope of this document.

- a) The following techniques (alone or in combination) should be considered for NDE of dissimilar welds during fabrication:
1. PT [prep, root pass, hot pass, cap pass, final inspection, and butter layer after PWHT (if applicable)];
 2. Angle beam UT* (SWUT or PAUT) on butt welds;
 3. UT on butter layer after PWHT (if applicable) to check bonding;
 4. RT;
 5. WFMT (magnetic materials only); and/or
 6. positive materials identification (PMI) can be used to confirm the chemical compositions of the different materials involved.
- b) In fired heater tubes, RT and UT* (shear wave or phased array) can be used.
- c) For inspection of cladding associated with dissimilar welds, UT* [straight beam or angle beam (SWUT or PAUT)] or ECT can be used.
- d) For inspection for creep damage due to DMWs, there is no reliable NDE method to detect creep in its early stages. Advanced stages can be detected using angle beam UT (SWUT* or PAUT*) or FMR. Destructive testing (removing a sample) to permit metallographic examination or stress-rupture testing may be applicable.
- e) For inspection for environmental cracking due to DMWs initiating on or near the ID surface exposed to the corrosive environment, PT or WFMT (for magnetic materials) on the internal surface or angle beam UT (SWUT* or PAUT*) from the external surface, can be used.

* DMWs (cladding, ferritic to austenitic butt welds, etc.) present challenges for inspecting due to beam/microstructure interactions (e.g. absorption, steering, and refraction). It is recommended that knowledge of grain size, specifically in austenitic stainless steels, and thickness are understood before applying UT techniques. Calibration should be done on similar materials (if not the same) as to be inspected. Inspection should be conducted by a technician experienced and knowledgeable with DMWs.

3.26.8 Related Mechanisms

Thermal fatigue (see 3.64), corrosion fatigue (see 3.21), creep and stress rupture (see 3.23), wet H₂S damage (see 3.67), and hydrogen stress cracking in HF (see 3.41).

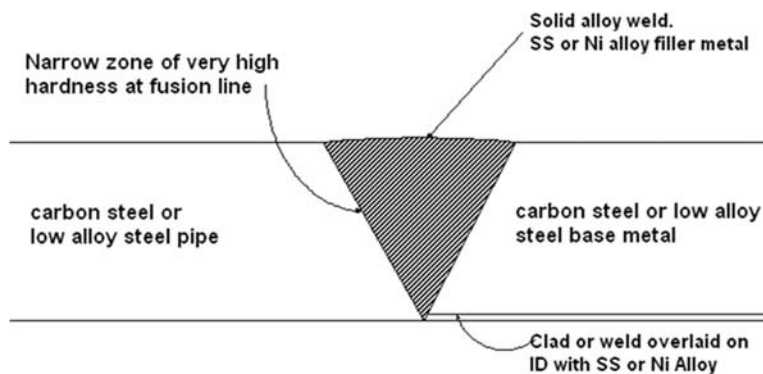
3.26.9 References

1. *Steam—Its Generation and Use*, 40th Edition, Babcock & Wilcox, 1992.
2. *Combustion: Fossil Power Systems*, Third Edition, Combustion Engineering, Windsor, CT, 1981.
3. H. Thielsch, *Defects and Failures in Pressure Vessels and Piping*, Krieger Publishing, Malabar, FL, 1977.
4. R.D. Port and H.M. Herro, *The Nalco Guide to Boiler Failure Analysis*, McGraw-Hill, New York, NY, 1991.
5. D.N. French, *Metallurgical Failures in Fossil Fired Boilers*, John Wiley and Sons, New York, NY, 1993.
6. B. Dooley and W. McNaughton, *Boiler Tube Failures: Theory and Practice*, 3 Volumes, EPRI, 1995.

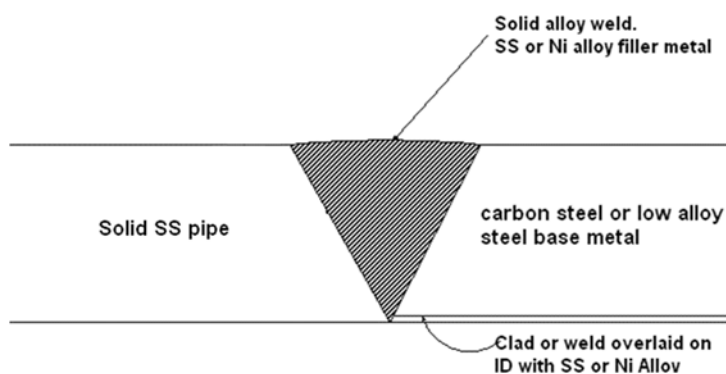
7. R.H. Ryder and C.F. Dahms, *Design Criteria for Dissimilar Metal Welds*, WRC Bulletin 350, Welding Research Council, Shaker Heights, OH, January 1990.
8. L.E. Penuela et al., "Analysis of Dissimilar Welds Exposed to High Temperature H₂/H₂S Conditions in a Hydrodesulfurizing (HDS) Unit," Paper No. 99383, *Corrosion/99*, NACE International, Houston, TX.
9. K.R. Lewis et al., "Assessment of Operating Limits for Critical Dissimilar Metal Welds in a Hydrocracker," Paper No. 01532, *Corrosion/2002*, NACE International, Houston, TX.
10. API 579-1/ASME FFS-1, *Fitness-For-Service*, American Petroleum Institute, Washington, DC, Second Edition, 2007.
11. API Recommended Practice 577, *Welding Inspection and Metallurgy*, American Petroleum Institute, Washington, DC.
12. API Subcommittee on Corrosion and Materials, Roundtable on Dissimilar Welds, April 17, 2007, Seattle, WA.
13. API Recommended Practice 582, *Welding Guidelines for the Chemical, Oil, and Gas Industries*, American Petroleum Institute, Washington, DC.
14. NACE SP0472, *Methods and Controls to Prevent In-service Environmental Cracking of Carbon Steel Weldments in Corrosive Petroleum Refining Environments*, NACE International, Houston, TX.
15. J.M. Mancini and M.A. Winters, "Cracking of a Dissimilar Metal Weld in Hydrogen Fluoride (HF) Acid Service," Paper No. 3794, *Corrosion/2014*, NACE International, Houston, TX.
16. "Integrity of Ferritic/Austenitic Dissimilar Welded Joints in Hydrogen Service," NIL Report #IN-98-32.
17. R. Avery, "Guidelines for Welding Dissimilar Metals," NiDi Report 14 018, Nickel Development Institute, Toronto, ON, Canada, 1991.
18. "Dissimilar-weld Failure Analysis and Development Program," EPRI Report CS-4252, Electric Power Research Institute, Palo Alto, CA, 1985.

Table 3-26-1—Coefficients of Thermal Expansion for Common Materials

Material	Coefficient (in./in./F x 10 ⁻⁶) to 800 °F (425 °C)
CS	7.97
1Cr-½Mo	7.53
2¼Cr-1 Mo	7.53
300 series SS	10.05
Alloy 600	8



(a)



(b)

Figure 3-26-1—Two primary DMW configurations.
 (a) Ferritic steel pipe (left) welded to clad or weld overlaid pipe.
 (b) Solid stainless steel pipe (left) welded to clad or weld overlaid pipe.

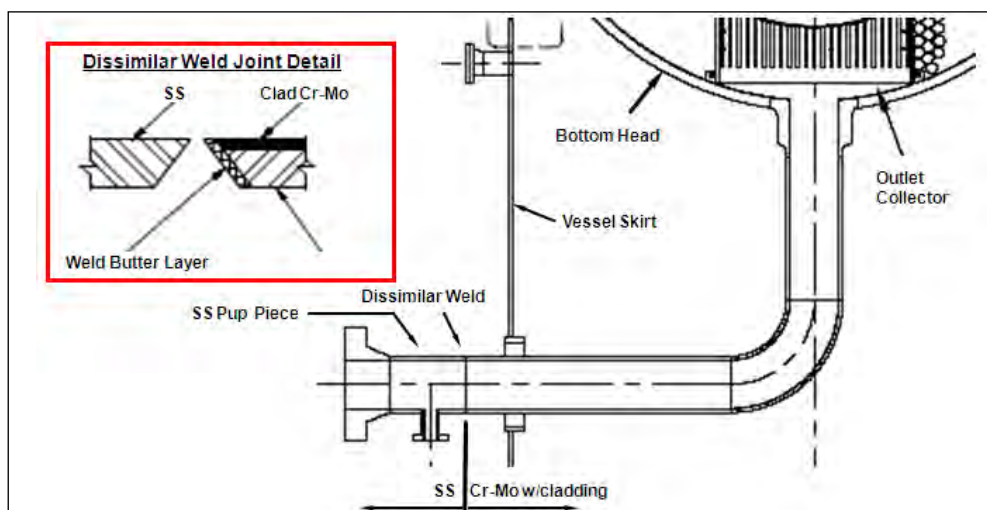


Figure 3-26-2—Schematic of typical weld detail used to join a solid stainless steel pipe to a clad or weld overlaid pipe. The sequence is as follows: (1) butter the weld bevel on the ferritic steel side, (2) perform PWHT of the ferritic side prior to making dissimilar weld, (3) complete the dissimilar weld using alloy filler metal, and (4) do not PWHT the completed dissimilar weld.



Figure 3-26-3—High-magnification photomicrograph of a DMW joining a ferritic alloy (SA213 T-22) used in high-temperature service. Creep cracks (black specks) can be observed in the ferritic alloy HAZs. Magnification 50X, etched.



Figure 3-26-4—Weld detail used to join a carbon steel elbow (bottom) to a weld overlaid pipe section (top) in high-pressure wet H₂S service. SSC occurred along the toe of the weld (arrow), in a narrow zone of high hardness.

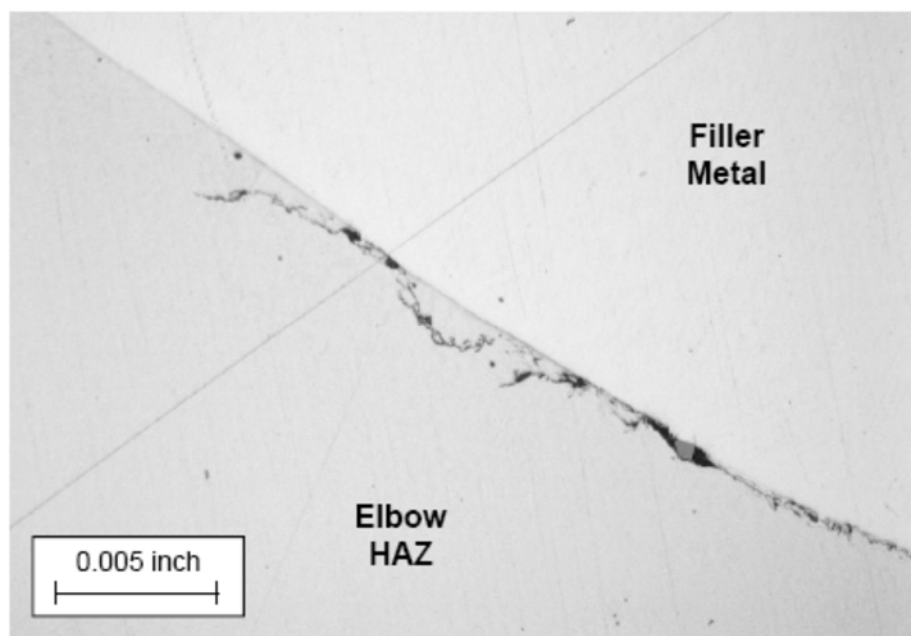


Figure 3-26-5—High-magnification photomicrograph of SSC in pipe section shown in Figure 3-25-4.

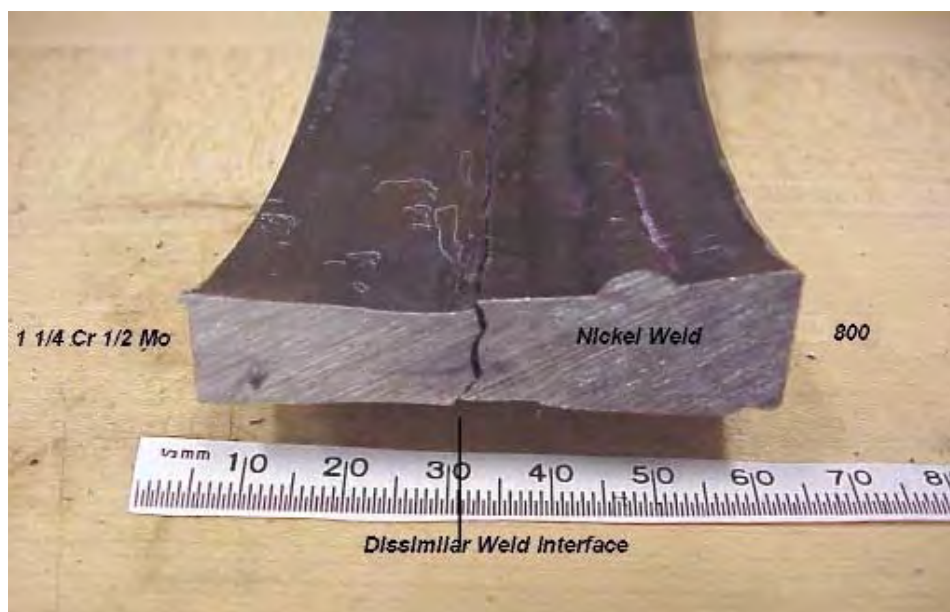


Figure 3-26-6—Failure of DMW joining 1.25Cr-0.5Mo to Alloy 800H in a hydro-dealkylation (HAD) reactor effluent exchanger. Crack propagation due to stresses driven at high of 875 °F (470 °C) and a hydrogen partial pressure of 280 psig (1.9 MPa).

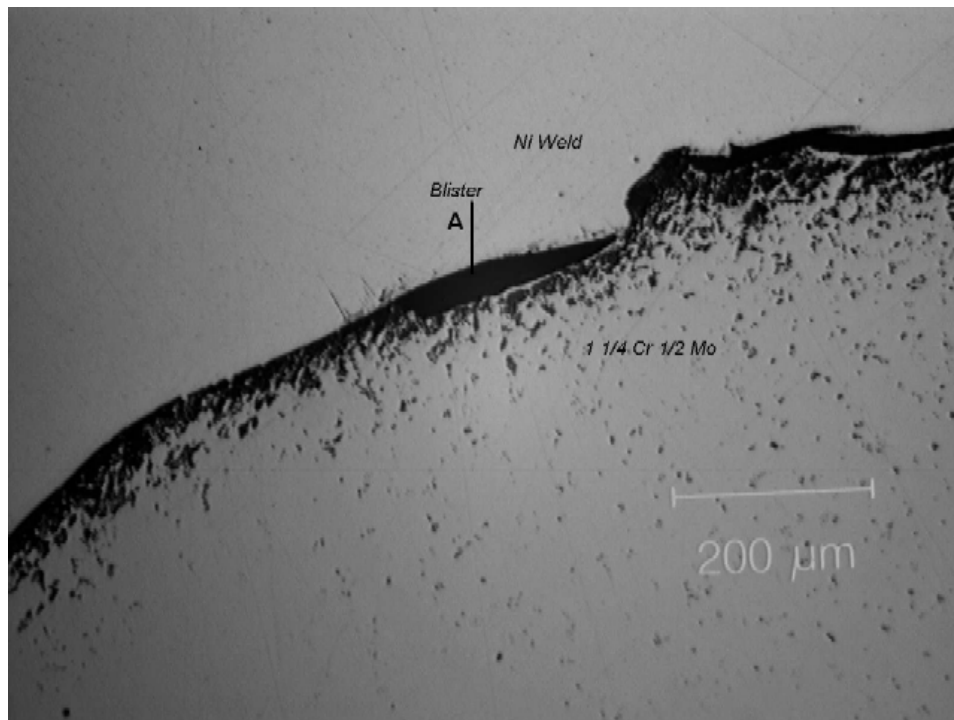


Figure 3-26-7—High-magnification photomicrograph of the crack in Figure 3-25-6 showing blistering and disbondment along the weld fusion line interface.

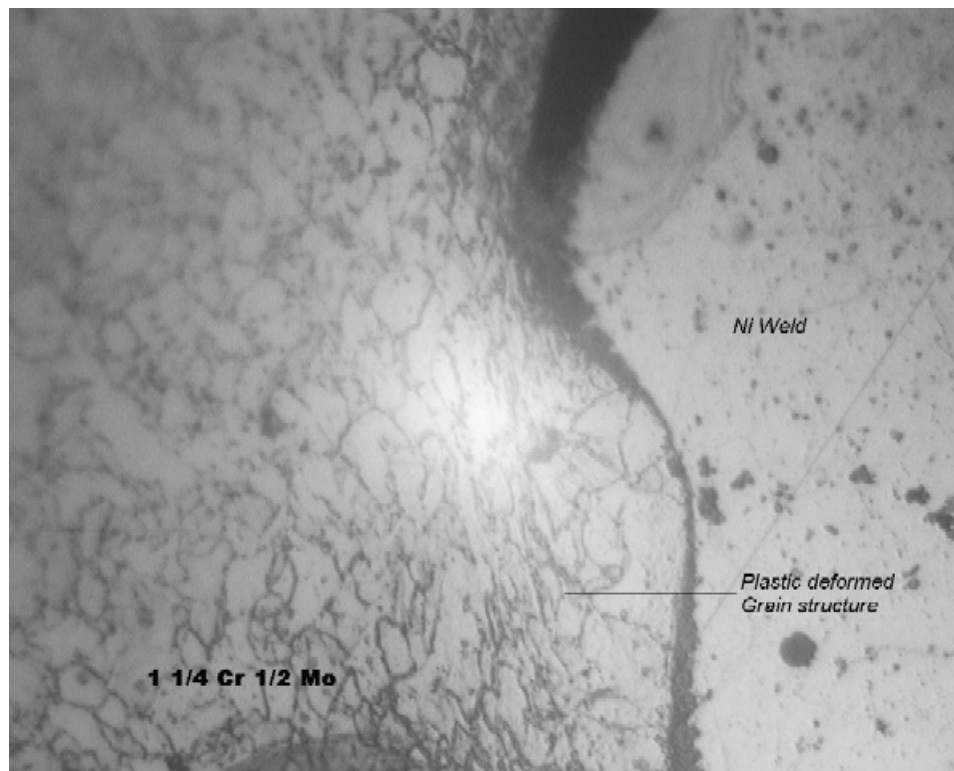


Figure 3-26-8—Higher-magnification photomicrograph of the crack shown above in Figure 3-25-6. Plastic deformation of the grain structure can be found at the vicinity of the blister.



Figure 3-26-9—Failure of nickel alloy DMW joining HP40 (Nb-modified) tube to 1.25Cr-0.5Mo flange in a steam-methane reformer due to cold hydrogen disbonding of the buttering layer. Process temperature 915 °F to 940 °F (490 °C to 505 °C), pressure 310 psig (2.15 MPa), H₂ content 10 % to 20 % (off-gas).

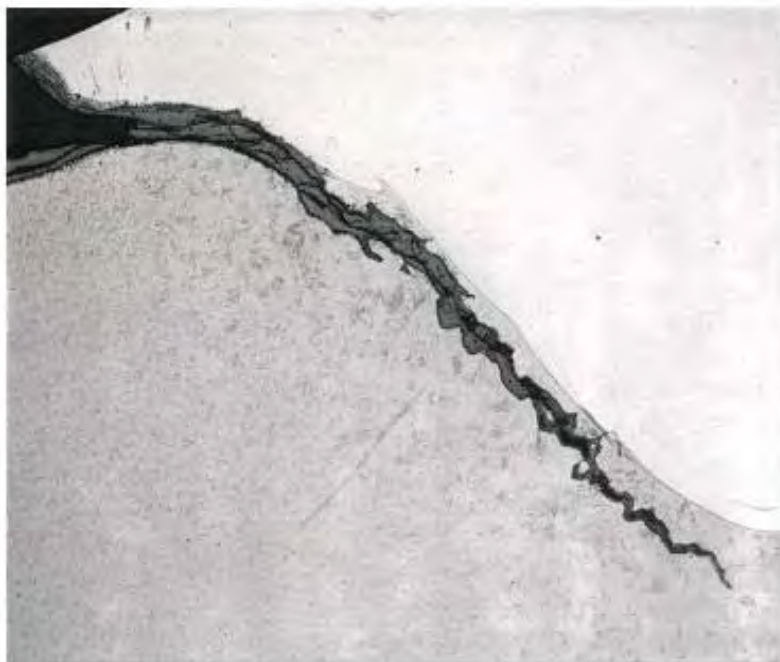


Figure 3-26-10—When both liquid phase coal ash corrosion and a DMW exists, stress-assisted corrosion of the 2.25Cr-1Mo HAZ may occur. Note that there is a lack of creep damage at the crack tip. Magnification 25X, etched.



Figure 3-26-11—A crack around the base of an Alloy 400 nozzle welded into a carbon steel vessel in HF acid service. (Reference 15)

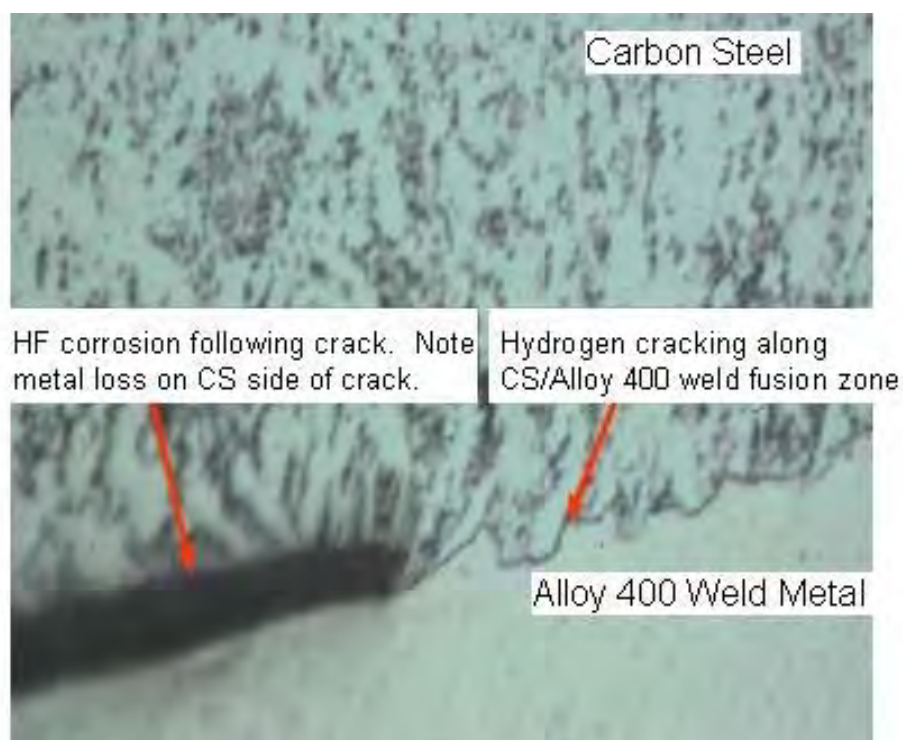


Figure 3-26-12—Photomicrograph showing crack propagation and corrosion in the Alloy 400 to carbon steel weld in Figure 3-25-11. (Reference 15)

3.27 Erosion/Erosion-Corrosion

3.27.1 Description of Damage

- a) This subject covers a wide range of situations of material loss, from flowing solid particles alone or in a liquid or vapor stream physically abrading the material to material loss accelerated by the flow of corrosive liquid or vapor possibly combined with the velocity-assisted removal of a protective film or scale.
1. Erosion is the mechanical removal of surface material as the result of relative movement between, or impact from, solids, liquids, vapor, or any combination thereof. It is typically found in services where solids are entrained in liquid or vapor streams such as slurries and fluidized solids. In refining, with the exception of water droplets in steam systems, it is unlikely that any flowing liquid or liquid impingement (without entrained solids) would be able to erode typical materials of construction without there also being a corrosion component present. The same can be said for gases, with the possible exception of steam cutting. However, see *Cavitation* (3.16).
 2. Erosion-corrosion is a description for the damage that occurs when particle erosion and/or high flow velocity contributes to corrosion by removing protective films or scales or otherwise accelerating the corrosion rate. This is also called velocity-assisted corrosion.
- b) In most refinery erosion-corrosion situations, corrosion is the dominant consideration.

3.27.2 Affected Materials

All metals, but mostly carbon steel and copper alloys in refining. Refractories are also affected. Most commonly affected are materials without true passivity, where the corrosion rate is limited by a protective corrosion layer or inhibitive film.

3.27.3 Critical Factors

- a) With solid particle mechanical erosion, metal loss rates will depend on the velocity and number of impacting particles (e.g. a low concentration of particles vs a slurry), as well as the size, shape, hardness, and density of the impacting particles, the hardness of the material subject to erosion, and the angle of impact.
1. Softer alloys such as copper and aluminum alloys that are easily worn from mechanical damage may be subject to severe metal loss under high-velocity conditions.
 2. Increasing the hardness of the eroding metal component can reduce the rate of erosion damage. However, this may not be effective where corrosion plays a significant role.
- b) For solids entrained in a liquid medium that also has a corrosion component, the same factors apply as with solid particle mechanical erosion described in Item a). However, with the solid particles removing any protective scales or other protective barrier on the metal surface, the rate of metal loss can be much greater than what is normally seen from the corrosion mechanism alone.
- c) For corrosive liquid droplets entrained in a vapor, metal loss rates will depend on the velocity and number or rate of impacting droplets and the corrosivity of the liquid.
- d) Many corrosive liquid environments will exhibit velocity-accelerated corrosion. In some cases, there is a threshold velocity below which corrosion is minimal but above which corrosion becomes significant. In other cases, there is no specific threshold; the highest corrosion rates simply occur where the velocity is greatest.
1. [Table 3-27-1](#) shows erosion-corrosion rates for a number of metals in seawater at different flow velocities. As the table illustrates, some alloys, particularly copper alloys, have an apparent threshold velocity above which the rate of metal loss increases significantly.

NOTE Increasing pipe thickness (schedule) will decrease the ID and increase the flow velocity, potentially increasing the corrosion rate.

- e) In most cases, the more corrosive the environment is to a particular material, the greater will be the erosion-corrosion effect, especially where the erosion effect damages the stability of a protective film, scale, or other barrier upon which the metal depends for its corrosion resistance. Any factors that contribute to an increase in corrosivity of the environment, such as temperature, pH, etc., can increase susceptibility to erosion-corrosion metal loss.

3.27.4 Affected Units or Equipment

- a) All types of equipment exposed to moving fluids and/or catalyst are subject to erosion and erosion-corrosion. This includes piping bends, elbows, tees and reducers, piping systems downstream of letdown valves and block valves, pumps, blowers, propellers, impellers, agitators, vessels with agitators, heat exchanger tubing, measuring device orifices, turbine blades, nozzles, ducts and vapor lines, scrapers, cutters, and wear plates.
- b) Erosion can be caused by gas-borne catalyst or coke particles or by particles carried by a liquid such as a slurry. This form of damage occurs as the result of catalyst movement in catalyst handling equipment (valves, cyclones, piping, reactors) and slurry piping in FCC reactor and regenerator systems. (Figure 3-27-1) It also occurs in coker heaters and coke handling equipment in both delayed and fluidized bed cokers. (Figure 3-27-2) And it causes “wear” on pumps (Figure 3-27-3), compressors, and other rotating equipment.
- c) Hydroprocessing reactor effluent piping may be subject to erosion-corrosion by ammonium bisulfide. The metal loss is dependent on several factors including the ammonium bisulfide concentration, H_2S and NH_3 partial pressures, velocity and shear stress on the pipe wall, and corrosion resistance of the material. (See 3.5.)
- d) Crude and vacuum unit piping and vessels exposed to naphthenic acids in some crude oils may suffer severe erosion-corrosion metal loss depending on the temperature, velocity, sulfur content, and naphthenic acid content. (See 3.46.)
- e) Erosion-corrosion is common in acid alkylation systems.
- f) Boiler water circuits can suffer accelerated corrosion from high-velocity flow, specifically known as “flow accelerated corrosion” (FAC). (See 3.9.)
- g) High velocity also increases cooling water corrosion rates as well as corrosion rates in other corrosive media, as described in their respective sections in this document.
- h) Erosion by water droplets in steam systems can be very damaging.

3.27.5 Appearance or Morphology of Damage

- a) Erosion and erosion-corrosion are typically characterized by a localized loss in thickness in the form of grooves, gullies, waves, rounded holes, valleys, or simply a greater amount of thinning in a localized area such as the outer radius of a piping elbow. These losses often exhibit a directional pattern.
 - 1. There have been cases where the erosion or erosion-corrosion has occurred over a large enough surface area to cause a rupture.
- b) In liquid lines containing particulate, low velocities, i.e. < around 5 fps (1.5 m/s), can allow solids to tumble to the bottom and cause erosion or erosion-corrosion in the 6 o'clock position.
- c) Failures can occur in a relatively short time.

3.27.6 Prevention/Mitigation

- a) Changes in shape, geometry, and materials can help mitigate erosion and erosion-corrosion. Examples include increasing the pipe diameter to reduce velocity, streamlining bends to reduce impingement, and using replaceable impingement baffles.

- b) Improved resistance to mechanical erosion is usually achieved by increasing component hardness, e.g. using a harder alloy, hardfacing, or a surface-hardening treatment. Erosion-resistant refractories in cyclones and slide valves have successfully resisted erosion.
- c) Erosion-corrosion is best mitigated by using more corrosion-resistant alloys and/or altering the process environment to reduce corrosivity, e.g. by deaeration, condensate injection, or the addition of inhibitors, as applicable. Resistance is generally not improved through increasing component hardness alone.
- d) Heat exchangers utilize impingement plates and occasionally tube ferrules to minimize erosion-corrosion problems.
- e) Refer to the relevant section of this document for methods to manage corrosion in erosion-corrosion prone environments (naphthenic acid, ammonium bisulfide, etc.).
- f) Ensure proper operation to avoid water droplets in the steam system.

3.27.7 Inspection and Monitoring

- a) Manual UT grids or automated scans can be used to determine the extent of erosion at susceptible areas, such as changes in direction, changes in diameter, or other turbulent areas. Randomly placed point UT readings may not be effective if they are not placed at the locations of potential susceptibility.
- b) Profile RT can be used to detect areas of erosion but may not be able to determine the actual remaining wall thickness. UT thickness is normally used as a follow-up technique to quantify wall loss.
- c) GWT can be used as a screening technique in certain applications where changes in piping direction will not impede the effectiveness of the examination.
- d) Permanently mounted thickness monitoring sensors can be used.
- e) Gouging or grooving along the bottom of a line and can be found by screening techniques [e.g. GWT, saturated low-frequency eddy current (SLOFEC), or X-ray crawler], UT scans or grids, or radiography.
- f) Infrared thermography scans can be used on stream to detect refractory degradation (potentially due to erosion).
- g) Specialized coupons can be used to determine if erosion is a potential concern.
- h) Sampling of process streams for chemical analysis of solids and particulate size can help determine erosion potential within a system.

3.27.8 Related Mechanisms

Cavitation ([3.16](#)).

3.27.9 References

1. *ASM Handbook—Corrosion*, Volume 13, ASM International, Materials Park, OH.
2. *ASM Handbook—Failure Analysis and Prevention*, Volume 11, ASM International, Materials Park, OH.

Table 3-27-1—Typical erosion-corrosion rates in seawater, mpy. (Reference 2)

Material	1 fps (tidal current)	4 fps (immersed in seawater flume)	27 fps (rotating disk)
Carbon steel	6	13	47
Cast iron	9	—	54
Silicon bronze	0.2	0.3	57
Admiralty brass	0.3	3	29
Hydraulic bronze	1	0.2	55
G bronze	1	0.3	46
Al bronze	1	—	44
Aluminum brass	0.4	—	19
90-10 Cu-Ni	1	—	16
70-30 Cu-Ni (0.05 %Fe)	0.3	—	32
70-30 Cu-Ni (0.5 % Fe)	<0.2	<0.2	6
Alloy 400	<0.2	<0.2	1
316 SS	0.2	0	<0.2
Alloy C-276	<0.2	—	0.05
Titanium	0	—	0

**Figure 3-27-1—Erosion-corrosion of a 1¼Cr-½Mo, 300-lb valve flange on an FCC catalyst withdrawal line.**



Figure 3-27-2—Erosion of a 9Cr-1Mo coker heater return bend as the result of high steam-air decoking velocity.



Figure 3-27-3—Erosion-corrosion of an ASTM A48 Class 30 cast iron impeller in a recycle water pump.

3.28 Ethanol Stress Corrosion Cracking

3.28.1 Description of Damage

Surface-initiated cracks caused by environmental cracking of carbon steel under the combined action of tensile stress and a fuel grade ethanol (FGE; ASTM D4806) or FGE/gasoline blend environment. Dissolved oxygen and the presence of variable stresses such as cyclic stress or component flexing increase the propensity for cracking.

3.28.2 Affected Materials

- a) All grades of carbon steel are susceptible.
- b) Ethanol SCC has not been reported in materials other than carbon steel, but general corrosion may be a concern with other materials including some alloys of aluminum, copper and copper alloys, lead, and zinc.
- c) FGE and blends with gasoline may adversely affect nonmetallic materials (e.g. coatings and seals), causing swelling, hardness changes, etc.

3.28.3 Critical Factors

- a) Several factors have been identified by field observations.
 - 1. Stress may be applied or residual. Highly stressed, locally cold worked components, or components with stress concentrators are susceptible to cracking. Variable stresses, such as those produced by loading and unloading of tanks, have led to cracking in tank bottoms and floating roofs.
 - 2. Cracking has been found to occur in FGE meeting ASTM D4806 specifications, including the water content requirement.
 - 3. Corrosion inhibitors may be added to ethanol to prevent general corrosion in vehicle fuel systems, but their effect on SCC is not fully understood.
- b) Other factors have been identified in controlled laboratory conditions using conservative slow strain rate test (SSRT) methods that stress the steel sample to failure. Evidence of SCC is based on the stress/strain behavior and an examination of the fracture surfaces.
 - 1. Aeration (i.e. the dissolved oxygen content) of the ethanol appears to be the most important factor for determining ethanol SCC susceptibility. Cracking has not been found under deaerated conditions.
 - 2. The maximum potential for ethanol SCC occurs within a narrow range of water content between 0.1 and 4.5 vol%.
 - 3. Ethanol SCC has been found to occur in blends of FGE and gasoline containing as little as 20 vol% FGE.
 - 4. Galvanic coupling of a new steel to corroded steel increases the likelihood of ethanol SCC.
 - 5. Increasing the chloride content of the ethanol tends to increase the severity of cracking and changes the crack type from the mainly intergranular found in the field to transgranular cracking.

3.28.4 Affected Units or Equipment

- a) Carbon steel storage tanks, rack piping, and associated equipment are susceptible to ethanol SCC. All grades of carbon steel are susceptible
- b) Cracking has also been reported in a pipeline used to transport FGE to and from a terminal.
- c) Ethanol SCC has not been reported in FGE manufacturers' equipment and tankage or in transportation equipment (barges, trucks, railcars).

- d) Cracking has not been reported in equipment handling FGE after it has been blended with unleaded gasoline at end-use concentrations (10 vol% FGE). There has been one reported failure of an end-user E-85 tank.

3.28.5 Appearance or Morphology of Damage

- a) Ethanol SCC is often found in the vicinity of welds and can appear as cracks that are parallel to the weld or transverse to the weld. ([Figure 3-28-1](#) to [Figure 3-28-8](#))
- b) Cracks are typically tight and may be filled with corrosion product.
- c) Ethanol SCC cracks are typically branched and intergranular, but transgranular or mixed-mode cracking has also been reported. Field failures tend to be intergranular, while laboratory testing has produced all crack morphologies. The cracking mode appears to depend on the chloride level, with an increased chloride content tending to shift the cracking from intergranular to transgranular or mixed mode.
- d) Microstructure of materials subjected to ethanol SCC are typically ferrite, or ferrite and pearlite.

3.28.6 Prevention/Mitigation

- a) The likelihood of ethanol SCC can be reduced though PWHT (when possible) or by applying coatings.
- b) Avoid designs with highly localized tensile stresses.
- c) Avoid the usage of lap seam welds (where practical) that may concentrate strain in components.
- d) Minimize cold working during fabrication and the use of springs and other devices (e.g. for floating roof components) made using cold-worked steel.

3.28.7 Inspection and Monitoring

Ethanol SCC is difficult to predict and detect, and as is generally the case for SCC mechanisms, routine inspection for ethanol SCC is not an effective way to manage the issue. Efforts need to be focused on prevention.

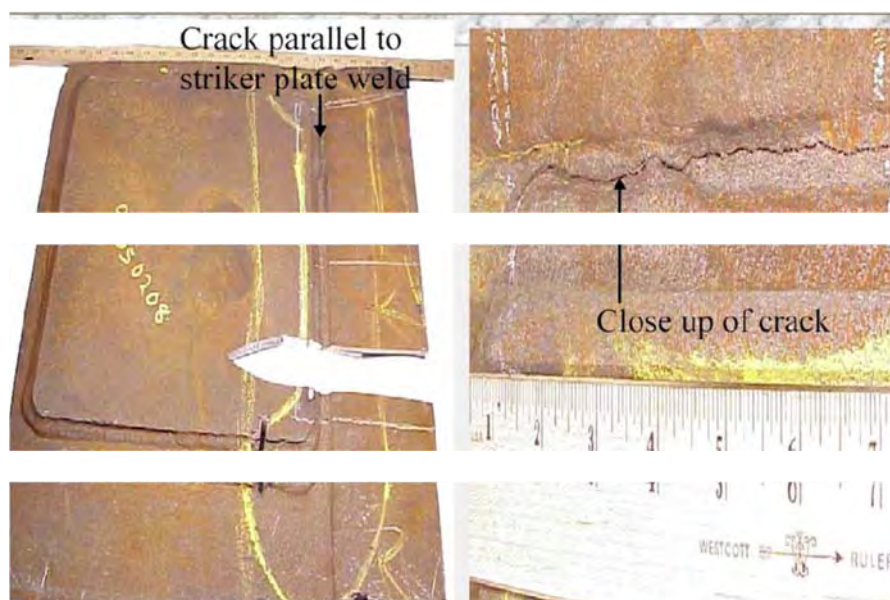
- a) Inspection for ethanol SCC is generally performed where cracking is already suspected or to determine the extent of cracking after a leak has occurred. It is especially difficult to detect prior to leaking in piping and equipment where there is no access to the internal surface. When inspection is performed, it should be focused on highly stressed areas, such as weld HAZs and the area immediately adjacent to the HAZ, highly cold worked areas, and highly stressed areas.
- b) It is difficult to visually detect ethanol SCC because the cracks are typically tight and filled with corrosion product. Some small leaks may occur before an ethanol crack can be visually detected.
- c) WFMT is the preferred method for detecting ethanol SCC. Methods for ethanol SCC inspection are similar to those used for detecting other types of SCC.
- d) Angle beam UT (SWUT or PAUT) can detect internal SCC from the external surface and thus can be used in instances where internal access for WFMT is not possible. These UT methods may also be used for estimating the depth of cracking.
- e) ACFM is an effective method for SCC detection and requires less surface preparation than WFMT.
- f) ECT is unproven as a method for detection of ethanol SCC.
- g) AET has had some success in detecting, locating, and monitoring SCC growth. However, results sometimes can be inconclusive and quality AET data may be difficult to obtain, and there is no industry track record of use of AET to detect ethanol SCC.

3.28.8 Related Mechanisms

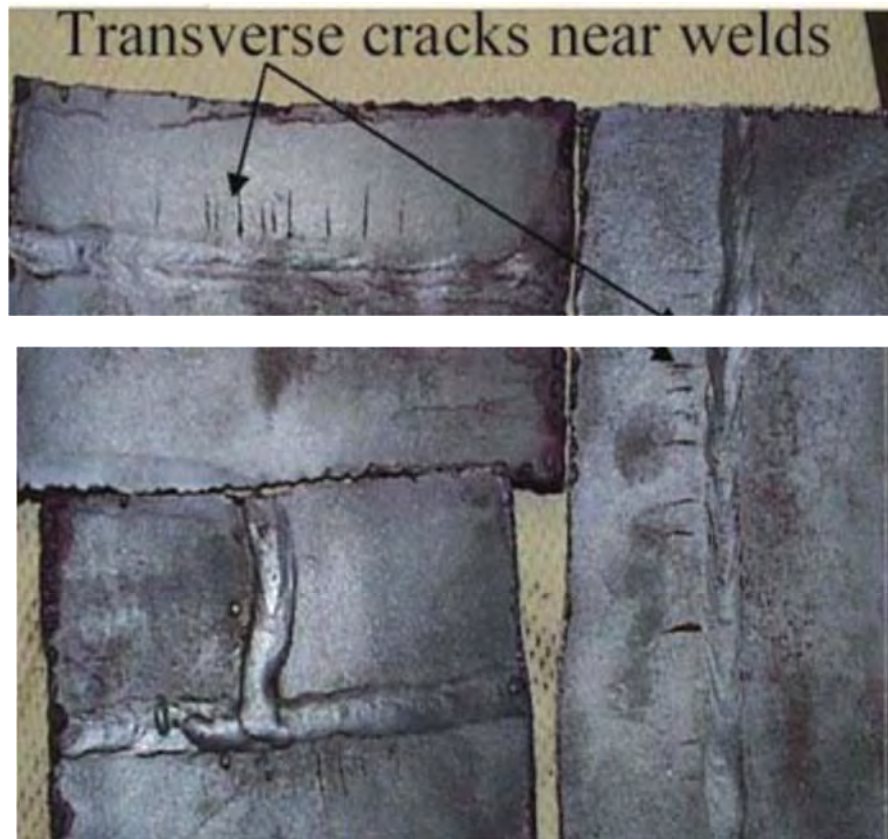
Ethanol SCC is assumed to be similar to SCC reported in methanol and various alkaline aqueous solutions, e.g. amine SCC (3.3), carbonate SCC (3.12), and caustic SCC (3.15).

3.28.9 References

1. API Technical Report 939-D, *Stress Corrosion Cracking of Carbon Steel in Fuel-grade Ethanol: Review, Experience Survey, Field Monitoring, and Laboratory Testing*, Second Edition, May 2007, American Petroleum Institute, Washington, DC.
2. API Bulletin 939-E, *Identification, Repair, and Mitigation of Cracking of Steel Equipment in Fuel Ethanol Service*, Second Edition, August 2013, American Petroleum Institute, Washington, DC.
3. ASTM D4806, *Standard Specification for Denatured Fuel Ethanol for Blending with Gasolines for Use as Automotive Spark-Ignition Engine Fuel*, ASTM International, West Conshohocken, PA.



**Figure 3-28-1—Ethanol SCC in a steel tank bottom.
Note crack running parallel to fillet weld in striker plate.**



**Figure 3-28-2—Ethanol SCC in a steel air eliminator vessel.
Note cracks running perpendicular to the weld.**



Figure 3-28-3—A leak in piping resulting from an ethanol stress corrosion crack adjacent to the weld.

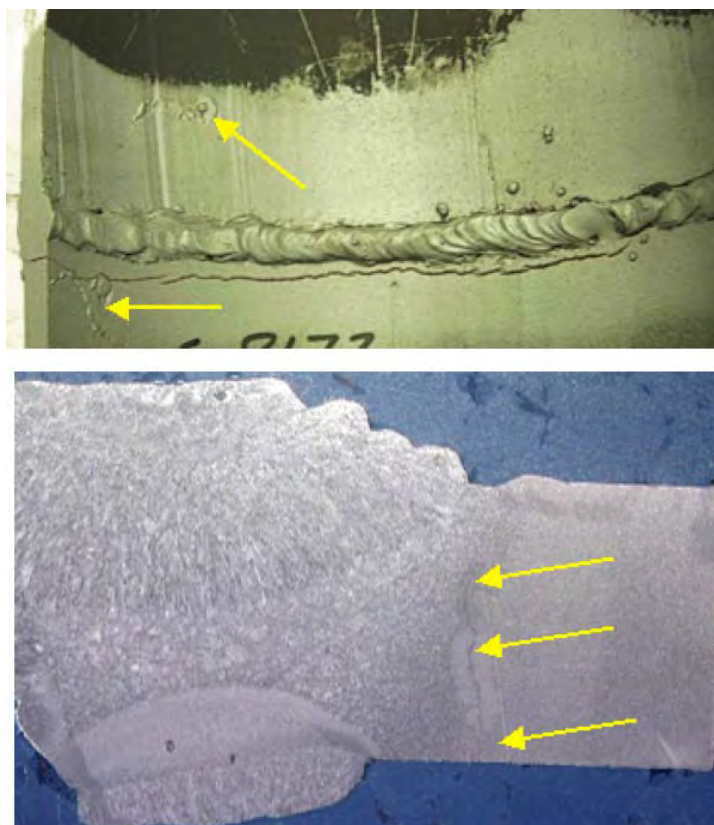


Figure 3-28-4—Ethanol SCC in steel pipe from a loading rack supply line. The top figure shows a 7-in.-long crack parallel to the weld root on the pipe ID surface. The bottom picture is a cross section of the above crack showing initiation outside the weld HAZ on the pipe's inside surface (Nital etch).



Figure 3-28-5—Ethanol SCC of steel piping in a fuel ethanol system return line/tank transfer line.
The top picture shows the crack parallels the pipe-to-tee circumferential weld. The bottom picture shows the inside and outside of the pipe after splitting and cleaning the weld area.
Parallel SCC cracks are clearly visible adjacent to the weld.

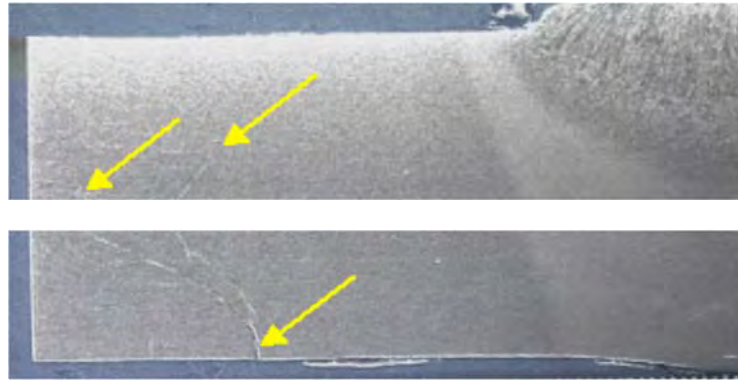


Figure 3-28-6—The top picture shows cracking initiating in the base metal on the ID of a section of piping adjacent to the weld. The bottom picture is a high-magnification photomicrograph of the crack above illustrating the predominately intergranular nature of the cracking. (Magnification 380X, Nital etch.)

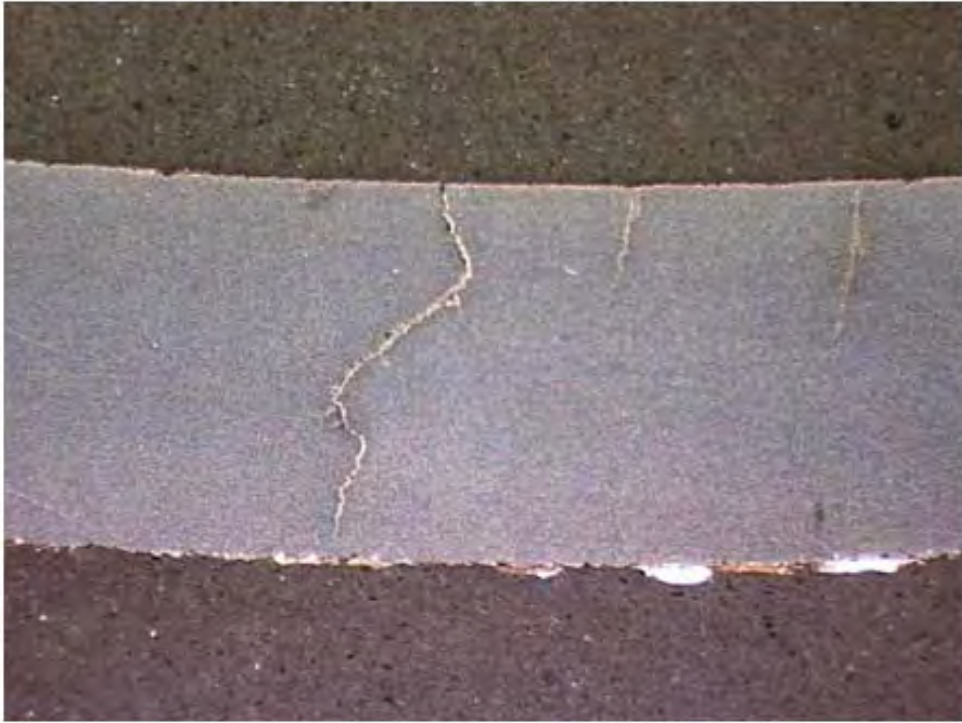


Figure 3-28-7—Transverse cross section of a piping section exposed to fuel ethanol showing multiple crack initiation sites characteristic of SCC.

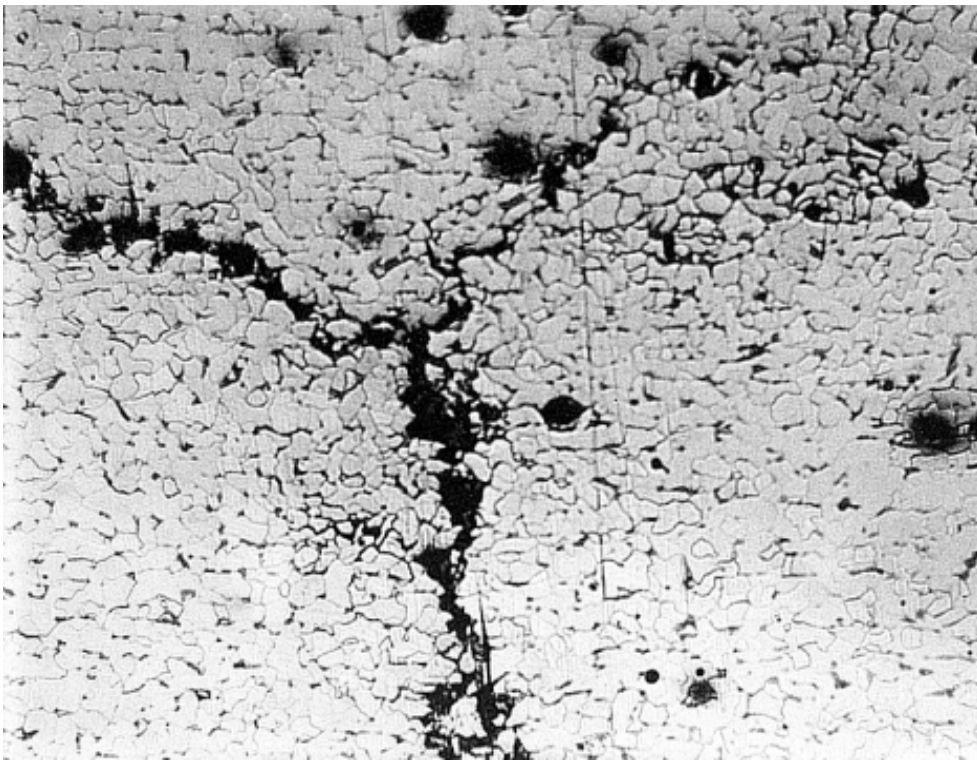


Figure 3-28-8—Photomicrograph of ethanol SCC in a steel tank bottom showing highly branched, intergranular cracks at 100X magnification.

3.29 Flue Gas Dew Point Corrosion

3.29.1 Description of Damage

Sulfur, nitrogen, and chlorine species in fuel will form sulfur dioxide, sulfur trioxide, nitrogen dioxide, and hydrogen chloride gas to go along with the CO₂ within the combustion products. At temperatures at or below the dew point, these gases and the water vapor in the flue gas will condense to form sulfurous acid, sulfuric acid, nitric acid, hydrochloric acid, and carbonic acid, which can lead to severe corrosion.

3.29.2 Affected Materials

Carbon steel, low-alloy steels, and 300 series SS.

3.29.3 Critical Factors

- a) The concentration of contaminants (sulfur, nitrogen, and chlorides) in the fuel and the operating temperature of flue gas metal surfaces determine the likelihood and severity of corrosion.
- b) Since all fuels contain some amount of sulfur, sulfuric and sulfurous acid dew point corrosion can occur if the metal temperatures are below the dew point.
- c) The dew point of sulfuric acid depends on the concentration of sulfur trioxide in the flue gas but is typically about 280 °F (140 °C).
- d) Dew points for sulfurous, hydrochloric, nitric, and carbonic acids depend on the concentrations of SO₂, HCl, NO₂, and CO₂ and on the water content of the flue gas, but they occur typically at temperatures lower than the water dew point, 212 °F (100 °C). Hence, corrosion by these acids gases is expected to occur only when surface temperatures reach or go below the water dew point.

3.29.4 Affected Units or Equipment

- a) Sulfur recovery unit (SRU) incinerators and FCC unit regenerator flue gas systems, as well as fired process heaters and boilers that burn fuels containing sulfur, nitrogen, or chloride have the potential for acid dew point corrosion in the economizer sections and in the stacks.
- b) Similar damage occurs in oil-fired boilers when the units are water-washed to remove ash if the final rinse does not neutralize the acid salts.
- c) Heat-recovery steam generators (HRSGs) that have 300 series SS feedwater heaters may suffer chloride-induced SCC from the gas side (OD) when the temperature of the inlet water is below the dew point of hydrochloric acid.
- d) 300 series SS feedwater heaters in HRSGs are potentially at risk if the atmosphere of the combustion turbine includes chlorine. Cooling tower drift from cooling towers that use chlorine-based biocides may blow into the combustion turbine and lead to potential damage in the feedwater heaters.

3.29.5 Appearance or Morphology of Damage

- a) Flue gas corrosion on economizers or other carbon steel or low-alloy steel components will have general wastage often with broad, shallow pits, depending on the way the acid condenses.
- b) For the 300 series SS feedwater heaters in HRSGs, SCC will have surface-breaking cracks and the general appearance will be somewhat crazed.

3.29.6 Prevention/Mitigation

- a) The metallic surfaces at the back end of the boilers and fired heaters and stacks should be kept at least 10 °F (6 °C) above the dew point temperature of sulfuric acid (the highest dew point of the condensable acid gases).

- b) For HRSGs, avoid the use of 300 series SS in the feedwater heaters if the environment is likely to contain chlorides.
- c) When water washing to remove ash, sodium carbonate should be added to the final rinse as an alkaline solution to neutralize the acidic ash constituents.

3.29.7 Inspection and Monitoring

Because flue gas corrosion occurs on tubes nearest the stack, which are typically finned tubes, the fins interfere with most inspection techniques that might be used on other heater and boiler tubes.

- a) Wall-thickness measurements by UT methods will monitor the wastage in affected tubes and stacks.
- b) To obtain UT thickness readings of finned tubes, a section of fins normally must be removed.
- c) Permanently mounted thickness monitoring sensors can be used.
- d) SCC of 300 series SS can be found using VT, PT, and ECT inspection.
- e) In the case where the tubes and fins are the same material, a VT of the fins will provide an indication if the damage mechanism is present.
- f) RT can be utilized to obtain thickness readings, as geometry allows.
- g) VT inside of stacks using a remote camera may be possible in some configurations.

3.29.8 Related Mechanisms

Hydrochloric acid corrosion ([3.37](#)), sulfuric acid corrosion, ([3.62](#)), and Cl^- SCC ([3.17](#)).

3.29.9 References

1. *Steam—Its Generation and Use*, 40th Edition, Babcock & Wilcox, 1992.
2. *Combustion: Fossil Power Systems*, Third Edition, Combustion Engineering, Windsor, CT, 1981.
3. H. Thielsch, *Defects and Failures in Pressure Vessels and Piping*, Krieger Publishing, Malabar, FL, 1977.
4. R.D. Port and H.M. Herro, *The Nalco Guide to Boiler Failure Analysis*, McGraw-Hill, New York, NY, 1991.
5. D.N. French, *Metallurgical Failures in Fossil Fired Boilers*, John Wiley and Sons, New York, NY, 1993.
6. B. Dooley and W. McNaughton, *Boiler Tube Failures: Theory and Practice*, 3 Volumes, EPRI, 1995.

3.30 Fuel Ash Corrosion

3.30.1 Description of Damage

- a) Fuel ash corrosion is accelerated high-temperature wastage of materials that occurs when contaminants in the fuel form deposits and then melt on the metal surfaces inside fired heaters, boilers, and gas turbines.
- b) Corrosion typically occurs with fuel oil or coal that is contaminated with a combination of sulfur, sodium, potassium, and/or vanadium.
- c) The resulting molten salts (slags) dissolve the surface oxide on the metal and enhance the transport of oxygen to the fresh surface to re-form the iron oxide at the expense of the tube wall or component.

3.30.2 Affected Materials

- a) All conventional alloys used for process heater and boiler construction are susceptible.
- b) Alloys of the 50Cr-50Ni family show improved resistance.

3.30.3 Critical Factors

- a) The concentration of molten salt-forming contaminants in the fuel, metal temperature, and alloy composition are the critical factors.
- b) Sodium (Na) and vanadium (V) content are very important. Typically, a combined concentration of Na and V above 50 ppm will cause damage.
- c) Corrosion occurs by this mechanism only if the metal temperature is high enough to melt the deposits and form the molten slag. It is most severe where the temperatures are the highest.
- d) The corrosion rates differ depending on the alloy and location within the heater.
- e) The molten slags are different for oil ash vs coal ash. They are also different for waterwall tube corrosion.
 - 1. For oil ash, the liquid species are mixtures of vanadium pentoxide and sodium oxide, or vanadium pentoxide and sodium sulfate. Depending on the precise composition, melting points below 1000 °F (540 °C) are possible.
 - 2. For coal ash, superheater and reheater corrosion is caused by sodium and potassium iron trisulfates that melt between 1030 °F and 1130 °F (545 °C and 610 °C), depending on the ratio of sodium and potassium. Reducing (low-oxygen) conditions, i.e. a flue gas rich in carbon monoxide, hydrogen sulfide, and hydrogen, will increase corrosion rates 2 to 5 times compared to oxidizing (oxygen-rich) conditions.
 - 3. For waterwall tube corrosion, the liquid species are mixtures of sodium and potassium pyrosulfates that have melting points as low as 700 °F (370 °C).
 - 4. Unburned coal particles also add carbon to the fly ash deposits and provide a reducing environment on the tube surface where corrosion occurs. Carburization of the tube surface, especially on austenitic alloys, will decrease corrosion resistance and increase tube wastage rates.

3.30.4 Affected Units or Equipment

- a) Fuel ash corrosion can occur in any fired heater, boiler, or gas turbine utilizing fuels with the aforementioned contaminants.
- b) Fuel ash corrosion is most often associated with fired heaters burning vanadium- and sodium-contaminated fuel oils or residue.

- c) Heater tubes are sometimes not affected because their skin temperatures in most heaters are cooler than the threshold melting point of the slags. Tube hangers and supports, however, operate hotter and can suffer severe fuel ash corrosion.
- d) Some gas turbines suffer blade corrosion when switched over to burning fuel oil.
- e) In some cases, coking of heater tubes may cause operators to increase heat flux that may push some components above the threshold temperature where fuel ash corrosion is possible.
- f) Since the melting points of these liquid species are around 1000 °F (540 °C) and higher in the superheaters and reheaters, any unit that has metal temperatures above the melting point of the sulfates may have the problem.
- g) For oil-fired boilers, fuel oils that do not contain vanadium are less prone to liquid fuel ash corrosion.
- h) For waterwall tubes, if the temperature can be maintained below the melting point of the pyrosulfates [i.e. below 700 °F (370 °C)], damage will be minimized. Thus, steam-generating pressures below about 1800 psi (12.5 MPa) are nearly immune.

3.30.5 Appearance or Morphology of Damage

- a) Oil ash corrosion is manifested as severe metal loss associated with slagging. In some cases, corrosion rates of 100 mpy to 1000 mpy (2.5 mm/yr to 25 mm/yr) may be experienced.
- b) With oil ash, corrosion may result in a corroded surface with numerous deep round pits. (Figure 3-30-1 and Figure 3-30-2)
 - 1. There are also representative photos of fuel ash and coal ash corrosion in Reference 4.
- c) The liquified corrodents can melt together during the corrosion process and form a hard, glassy, tenacious scale.
- d) With coal ash, the appearance will be a smooth interface between a glassy slag layer and the metal.
- e) Metallographic examination and deposit-analysis techniques can be used to verify the presence of fuel ash corrosion. Oil ash deposit will often appear in at least two distinct layers. The deposit adjacent to the component will have a dark gray or black appearance at room temperature.
- f) For waterwall tubes, thermal fatigue cracks can occur in conjunction with the fuel ash corrosion. (Figure 3-30-3) The cracks are predominantly circumferential and, to a lesser extent, axial. The overall appearance on the waterwalls is one of circumferential grooving.
 - 1. After the liquid ash layer develops, the “slush” can only hold a certain weight of ash. When the weight is excessive, the slag is shed, exposing a bare, uninsulated tube to the heat flux of the firebox. The temperatures will spike on waterwall tubes, by perhaps 100 °F (55 °C). Repetitive cycles can result in thermal fatigue cracking.
 - 2. The mechanism for the steam-cooled tubes is similar, except that the temperature spike is probably less, and therefore the thermal fatigue damage is less severe.
 - 3. After removal of the corrosion scale on superheaters and reheaters, the steel can have an alligator-hide appearance. (Figure 3-30-4) This, as well as the circumferential cracking on waterwalls in coal-fired boilers, is caused by a similar mechanism.

3.30.6 Prevention/Mitigation

- a) Fuel ash corrosion can be prevented by blending or changing fuel sources (minimizing the contaminants) and by operating equipment so that hot components are below the temperature where molten deposits are formed.
- b) Proper burner design and burner management can help to reduce flame impingement and localized hot spots.
- c) In some cases, the characteristics and melting points of the slags can be changed by firing with low excess oxygen or by injecting special additives into the fuel. These changes can increase the melting point of the slags and reduce the tendency of the deposits to stick to metal surfaces or dissolve the protective oxide scale. Even with changes to reduce slag formation, corrosion may continue if metal surfaces are not cleaned to remove slag and corrosion products.
- d) Corrosion of some components, such as tube hangers and supports, can be minimized by changing to a 50 %Cr to 50 %Ni alloy, such as Alloy 657. Designs of tube hangers may need to be modified to account for the lower stress-rupture strength of the 50Cr-50Ni alloys.
- e) Maintaining the combined sodium plus vanadium content below 50 ppm will control the damage.

3.30.7 Inspection and Monitoring

- a) VT is usually sufficient to detect fuel ash corrosion.
- b) Metal loss is likely to be severe, and the presence of a slag will be apparent.

NOTE Tubes may need to be grit blasted in order to remove the tenacious, glass-like deposit.

- c) UT may be useful to measure loss of thickness.

3.30.8 Related Mechanisms

Hot corrosion, hot ash corrosion, molten salt corrosion, oil ash corrosion, and coal ash corrosion are all terms used to describe this mechanism.

3.30.9 References

1. *Steam—Its Generation and Use*, 40th Edition, Babcock & Wilcox, 1992.
2. *Combustion: Fossil Power Systems*, Third Edition, Combustion Engineering, Windsor, CT, 1981.
3. H. Thielsch, *Defects and Failures in Pressure Vessels and Piping*, Krieger Publishing, Malabar, FL, 1977.
4. R.D. Port and H.M. Herro, *The Nalco Guide to Boiler Failure Analysis*, McGraw-Hill, New York, NY, 1991.
5. D.N. French, *Metallurgical Failures in Fossil Fired Boilers*, John Wiley and Sons, New York, NY, 1993.
6. B. Dooley and W. McNaughton, *Boiler Tube Failures: Theory and Practice*, 3 Volumes, EPRI, 1995.
7. API Recommended Practice 573, *Inspection of Fired Boilers and Heaters*, American Petroleum Institute, Washington, DC.
8. E. Mirabel et al., "Fireside Carburization of Stainless Steel Furnace Tubes," Paper No. 99080, *Corrosion/99*, NACE International, Houston, TX.



Figure 3-30-1—Type 316Ti stainless steel roof tube in a heavy fuel oil-burning vacuum heater that failed by fuel ash corrosion. The tube perforated at this location.



Figure 3-30-2—A closer view of the pitting appearance of the attack on the tube surface shown in Figure 3-29-1.

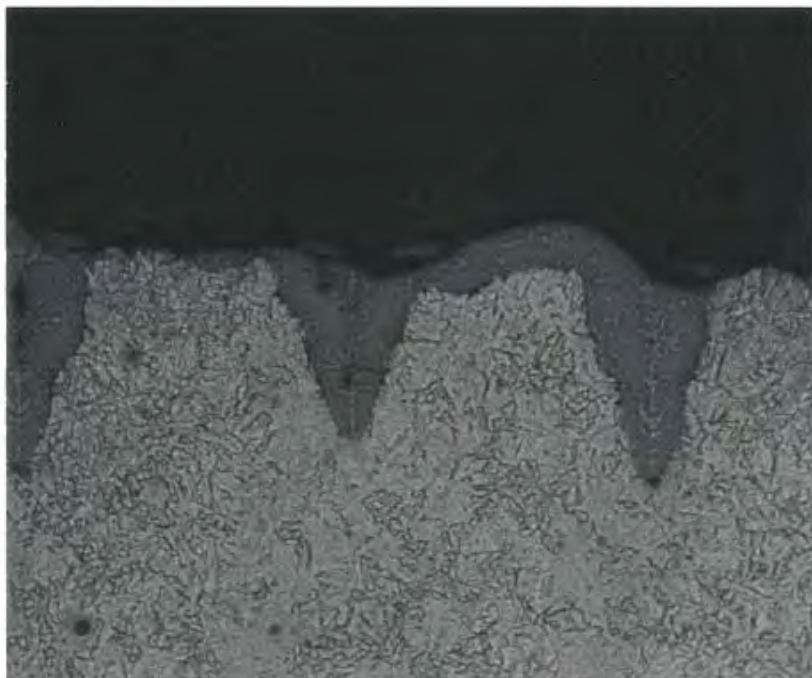


Figure 3-30-3—In cross section, the surface grooving on waterwall tubes that occurs in conjunction with fuel ash corrosion appears as broad, V-shaped corrosion fatigue cracks. Magnification 100X, etched.



Figure 3-30-4—The “alligator hide” morphology of liquid coal-ash corrosion is evident on the metal surface when the dense, glassy deposit is removed. Magnification 2.4X.

3.31 Galvanic Corrosion

3.31.1 Description of Damage

Accelerated corrosion that can occur at the junction of dissimilar metals when they are joined together in a suitable electrolyte, such as a moist or aqueous environment or soils containing moisture.

3.31.2 Affected Material

All metals with the exception of most noble metals.

3.31.3 Critical Factors

- a) For galvanic corrosion, three conditions must be met.
 1. There must be two (or at least two) different metals with different electrochemical potentials.
 2. The dissimilar metals must be electrically coupled together, either by being directly in contact with or connected to each other or connected by a wire or other conductor. One of these metals is known as the anode and the other is the cathode.
 3. Both metals must be immersed or in contact with the same, continuous electrolyte, i.e. a fluid that can conduct electric current. Moisture or a separate water phase is usually required for the fluid to have enough conductivity.
- b) The more noble material (the cathode) is protected by sacrificial corrosion of the more active material (the anode). The anode corrodes at a higher rate than it would if it were not connected to the cathode.
- c) A typical listing of the relative position on the active to noble scale of alloys in seawater is shown in [Table 3-31-1](#).
- d) The farther the alloys are apart in the table, the higher the driving force for corrosion.
- e) The relative amount of surface area exposed to the electrolyte between the more active anode material and the more noble cathode material has a significant affect.
 1. If there is a small anode-to-cathode exposed surface area ratio, the corrosion rate of the anode can be very high.
 2. If there is a large anode-to-cathode surface area ratio, the corrosion rate of the anode will be less affected.
- f) The same metal may act as either an anode or a cathode in different situations due to the effect of surface films, scale, and/or the properties of the electrolyte on its electrochemical potential in that particular situation (e.g. old steel pipe connected to new steel pipe).
- g) The same electrochemical coupling of different metals that leads to galvanic corrosion is put to beneficial effect in the form of cathodic protection when a more active sacrificial material, e.g. an aluminum or magnesium anode, is coupled to a less active (more noble) metal, e.g. carbon steel. This is the principle behind galvanized steel, where the zinc (Zn) coating corrodes preferentially to protect the underlying carbon steel. [If there is a break in the galvanizing coating, the resulting large anode to small cathode area prevents accelerated corrosion of the steel, while the Zn coating (anode) continues to cathodically protect the exposed steel.] This Zn-to-steel anode-to-cathode relationship appears to reverse in aerated water at temperatures above about 150 °F (65 °C). This is because the corrosion products and scale that form on the surface of the galvanizing make the surface more noble than steel. However, the relative positions of the open circuit potentials of the two metals do not actually switch at any temperature.

3.31.4 Affected Units or Equipment

- a) Galvanic corrosion can occur in any unit where different metals are coupled in a conductive fluid. Heat exchangers are susceptible if the tube material is different from the tubesheet and/or baffles, particularly if saltwater cooling is utilized.
- b) Buried piping and ship hulls are also typical locations for galvanic corrosion.

3.31.5 Appearance or Morphology of Damage

- a) Damage occurs where two different materials are joined at welded, bolted, or rolled connections.
- b) The more active material can suffer generalized loss in thickness or more aggressive localized loss adjacent to the point of connection, with the appearance of crevice, grooving, or pitting corrosion, depending on the driving force, conductivity of the electrolyte, and the relative anode/cathode area ratio. (Figure 3-31-1 and Figure 3-31-2)

3.31.6 Prevention/Mitigation

- a) The best method for prevention or mitigation is through good design.
- b) Coupling of different metals in a conductive fluid should be avoided; however, the galvanic effect will be minimized if the anode/cathode surface area ratio is favorable.
- c) If a coating is to be used to mitigate corrosion of a galvanic couple, care must be exercised. If only the active material were coated, a small anode-to-cathode area ratio would exist wherever a coating defect or damage exposed bare anode metal, which would greatly accelerate corrosion of the anode at the break in the coating. Therefore, the exposed areas of both the anode and the cathode should be coated. If only one can be coated, the more noble cathode material should be the one coated. In this case the coating will not protect the anode, but at least the acceleration of the corrosion rate caused by the galvanic couple will be minimized or eliminated.
- d) For piping, specially designed electric insulating bolt sleeves and gaskets (i.e. isolation flanges) can eliminate the electrical connection.
- e) Sacrificial anodes are sometimes installed in carbon steel cooling water exchanger channels to control channel and tubesheet corrosion, particularly where Cu-alloy tubes such as admiralty brass are used.

3.31.7 Inspection and Monitoring

- a) VT and UT thickness gauging are effective methods for detecting galvanic corrosion.
 - 1. VT may indicate loss of the more anodic material by displaying oxidized material before it is cleaned.
 - 2. UT thickness measurement techniques have been effective in determining the amount of loss in the more anodic material.
- b) Permanently mounted thickness monitoring sensors can be used.
- c) The damage could also be hidden underneath a bolt or rivet head.
 - 1. An initial "total picture" examination may be necessary to understand the nature of joints under consideration. In the case of bolt heads or rivets, an angled beam technique may be needed to evaluate the hidden loss under the head of the fastener.

3.31.8 Related Mechanisms

Concentration cell corrosion (3.19), soil corrosion (3.57), DMW cracking (3.26), and titanium hydriding (3.66).

3.31.9 References

1. *Corrosion Basics—An Introduction*, NACE International, Houston, TX, 1984, pp. 33–37.

Table 3-31-1—Galvanic Series in Seawater. (Reference 1)

Corroded End—Anode—More Active
Magnesium
Magnesium alloys
Zinc
Aluminum
Aluminum alloys
Steel
Cast iron
Type 410 SS (active state)
Ni-resist
Type 304 SS (active state)
Type 316 SS (active state)
Lead
Tin
Nickel
Brass
Copper
Bronze
Copper-nickel
Monel
Nickel (passive state)
Type 410 SS (passive state)
Type 304 SS (passive state)
Type 316 SS (passive state)
Titanium
Graphite
Gold
Platinum
Protected End—Cathode—More Noble

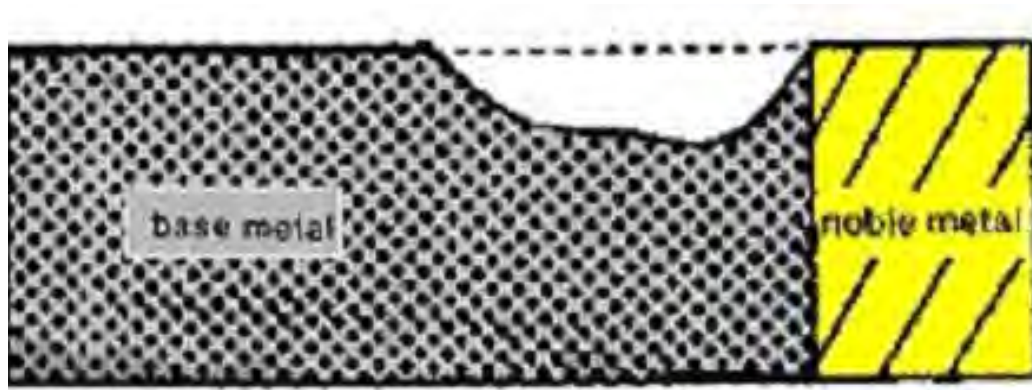


Figure 3-31-1—Preferential galvanic corrosion of the more active of the two materials.

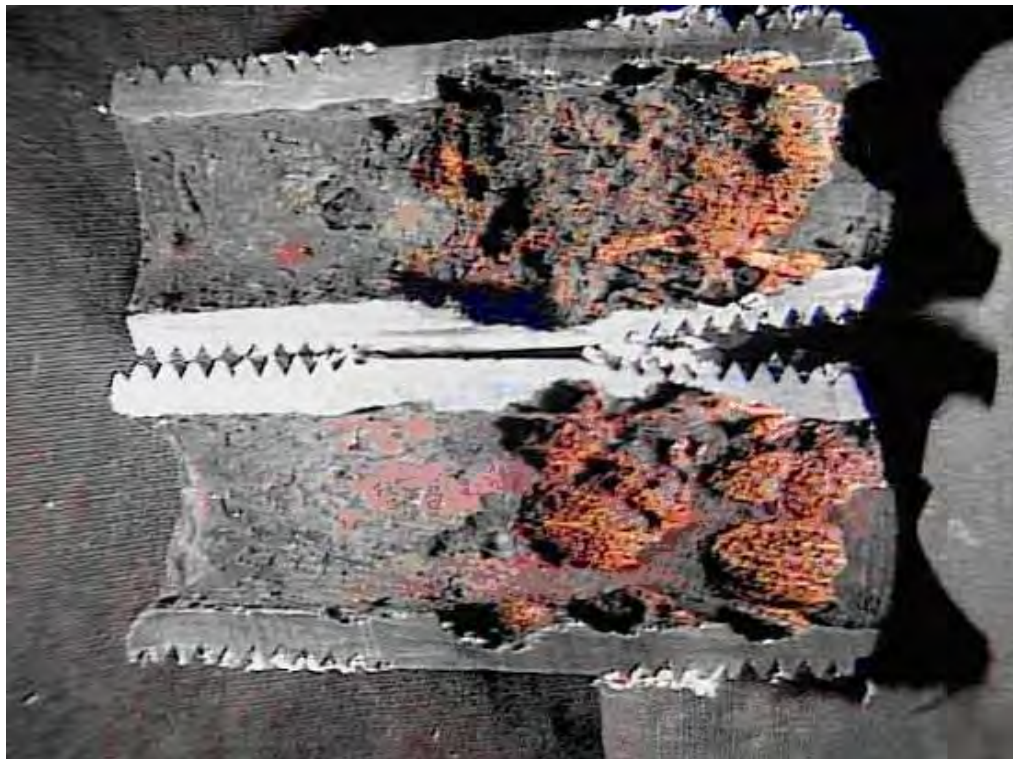


Figure 3-31-2—Galvanic corrosion of a carbon steel nipple in a stainless steel vessel in warm water service.

3.32 Gaseous Oxygen-enhanced Ignition and Combustion

3.32.1 Description of Damage

Many metals are flammable in oxygen and oxygen-rich air (>25 % oxygen) services even at low pressures, whereas they are non-flammable in air. The spontaneous ignition or combustion of metallic and nonmetallic components can result in fires and explosions in certain oxygen-rich gaseous environments if not properly designed, operated, and maintained. Once ignited, metals and non-metals burn more vigorously with higher oxygen purity, pressure, and temperature.

3.32.2 Affected Materials

- a) Carbon steels and low-alloy steels are flammable in oxygen-rich environments greater than about 15 psig (0.1 MPa) oxygen pressure. However, with special precautions, these materials are safely used in high-pressure oxygen.
- b) 300 series SS have better resistance to low-pressure oxygen-rich environments and are generally difficult to ignite at oxygen pressures below about 200 psig (1.4 MPa).
- c) Copper alloys (with > 55 % copper) and nickel alloys (with > 50 % nickel) are very fire resistant and are generally considered non-flammable. Because of their excellent oxygen “compatibility,” they are often selected for impingement and turbulent services such as valves and instrumentation. (But, see [Figure 3-32-5](#).) Alloy 400 is highly resistant.
- d) Although widely used for oxygen cylinders and in oxygen manufacturing plants, aluminum is usually avoided for flowing oxygen. Aluminum may ignite at ambient temperature with low levels of ignition energy. If ignited, it burns quickly and with a large energy release.
- e) The easiest materials to ignite are plastics, elastomers, and hydrocarbon lubricants, and their use is minimized in oxygen systems.
- f) Titanium and titanium alloys are generally avoided in oxygen and oxygen-rich service, because they have low ignition energies and release a large amount of energy during combustion. Tests indicate that titanium can sustain combustion at oxygen pressure as low as 1 psia (7 kPa). Most industry documents caution against the use of titanium in oxygen systems. (References 5 and 6)

NOTE These are general guidelines and should not be considered for design.

3.32.3 Critical Factors

Many factors contribute to the likelihood of combustion and ignition in oxygen services. They include system pressure, line velocity, temperature, system cleanliness, piping configuration, component thickness, system design, oxygen content of the stream, and ignition energy. (A unique aspect of oxygen-rich systems is that the source of energy does not need to be a spark or flame; the source may be the presence of ignition energy.)

- a) Pressure in an oxygen system affects the potential ignition mechanisms of metallic systems. Systems operating below 500 psi are considered less severe than systems operating above 500 psi.
 - 1. High-purity oxygen systems over 500 psi are considered to have a severe effect on metal burning reactions because the amount of energy needed to start ignition is lower than the energy required in low-pressure systems.
 - 2. High-purity oxygen systems below 500 psi are considered to have a moderate or mild effect on metal burning reactions.
- b) The primary concern with high-velocity oxygen flow is the entrainment of particulates in the stream. High-velocity particulates can create friction or impinge on a surface, such as at a pipe bend. Friction or impingement could result in ignition of the metal. Oxygen velocities in carbon steel and stainless steel piping should comply with industry limits as shown in Reference 1. Allowable velocity is a function of pressure and flow condition (direct impingement or non-impingement).

- c) The temperature of a material affects its flammability. As temperature increases, a lower amount of additional energy is required for ignition and sustained combustion. The effect of temperature is most critical on nonmetallic components of an oxygen system. The minimum temperature at which a substance will support combustion, under a specific set of conditions, is referred to as the ignition temperature. Published ignition temperatures for most alloys are near the alloy's melting temperature. However, these are measured in non-flowing conditions. Actual systems can suffer ignition and combustion at room temperature (and lower) due to particle impact and other mechanisms.
 - 1. Commonly used metals in high-purity oxygen systems may have an autoignition temperature as low as 1650 °F (900 °C).
 - 2. Nonmetallic items in high-purity oxygen systems may have an autoignition temperature as low as 300 °F (150 °C).
- d) System cleanliness is important for the safe operation of oxygen systems. Contamination with metallic fines or hydrocarbons such as oils and greases during construction or maintenance activities can lead to fires during subsequent start-up of the unit. These materials are easy to ignite and can lead to a large fire and breach of the system.
- e) The piping configuration, or layout, could create impingement areas such as at elbows, tees, or valves. These components pose a higher risk of ignition than straight pipe.
 - 1. Particles in the flowing oxygen can strike these areas and cause ignition.
 - 2. Operation of valves and regulators (opening/closing) causes high turbulence and impingement.
 - 3. Material selection for components in impact or impingement prone locations and high-turbulence areas is critical.
 - 4. Only items selected and cleaned specifically for oxygen service should be used in high-purity oxygen systems.
- f) Thin components or components with a high ratio of surface area to material volume provide a geometry that is susceptible to ignition of the metal. Examples include mist eliminators, demister pads, steel wool, and structured packing. (Figure 3-32-4)
- g) The system design must compensate for the effect of items like mechanical impact, heat of combustion, kindling effect of contaminants, system resonance, fresh metal exposure, heat of compression, and turbulence. Reference 7 provides detailed information on the compatibility of various metals in oxygen-rich environments.
- h) The oxygen content has two effects. As the concentration of oxygen increases, the likelihood and intensity of a possible reaction increases. Also, as the oxygen increases, there is more available to support combustion during the oxidation reaction with the system material(s).
- i) Ignition energy in oxygen-rich environments can be derived from many sources. The heat of compression due to rapid pressure increases, the exothermic reaction resulting from the high rate of oxidation of some materials, or simply the available heat energy in the presence of low-ignition-temperature materials can cause items in oxygen-rich environments to ignite.

3.32.4 Affected Units or Equipment

- a) These guidelines apply to any unit that uses oxygen or enriched air for combustion or other process reasons.
- b) Oxygen is sometimes used in SRUs (Figure 3-32-1 to Figure 3-32-3), FCC units, gasification units, and partial oxidation (POX) units.

- c) Oxygen piping systems, especially valves, regulators, and other impingement areas, are potentially vulnerable. Non-metals such as those used for seats and seals are easier to ignite than metals. (Figure 3-32-6)

3.32.5 Appearance or Morphology of Damage

- a) The worst situation is when the pressure envelope is breached because of fire. In that case, the appearance is obvious. Oxygen fires can cause significant burning of metal components and extensive structural damage. (Figure 3-32-4).
- b) Visible external heat damage (glowing pipe or heat tint) is a strong indication of an internal fire. This can be caused by accumulation of flammable debris at a low point or other location and combustion or smoldering of the debris.
- c) In some cases, a small component such as a valve seat will burn without kindling other materials and without any outward sign of fire damage. It is noticed when the component is removed because it is not functioning properly.

3.32.6 Prevention/Mitigation

Refer to industry-recommended guidelines included in the references listed below. Some general considerations are as follows.

- a) Oxygen fires are a sudden occurrence and not a progressive degradation or weakening of the material. Prevention is best accomplished by keeping systems clean and thoroughly cleaning them after maintenance or inspections.
- b) Maintain velocity within recommended limits. If practical, avoid velocities that are nominally above 100 fps (30 m/s) in gaseous oxygen.
- c) Ensure that replacement components are suitable for oxygen service.
- d) Minimize lubricants and use only “oxygen-compatible” lubricants.
- e) Do not unnecessarily open oxygen systems for visual or other inspections as this could introduce contamination.
- f) A thorough review is needed before modifying oxygen systems to operate at higher pressures, temperatures, or velocities.
- g) Minimize sudden changes in pressure in the system. If high-pressure oxygen suddenly enters a system initially at low pressure by quick operation of a valve, the “dead end” of that system experiences heating from adiabatic compression of the oxygen. Adiabatic compression heating can ignite plastics and rubbers but will not ignite metals. Valve seats, seals, nonmetallic hoses, etc., can be ignited by this mechanism.
- h) Avoid the use of plastic pipe in oxygen piping systems.

3.32.7 Inspection and Monitoring

- a) Most commercial oxygen is dry and non-corrosive at normal ambient temperatures. Because of the sudden catastrophic ignition of metals under certain conditions, this type of damage cannot be inspected for in advance.
- b) Tell-tale signs of a minor fire such as external heat damage or signs of malfunctioning valves or other components containing nonmetallic components may be indicative of a problem.
- c) Blacklights can be used to check for hydrocarbon contamination.

3.32.8 Related Mechanisms

None.

3.32.9 References

1. CGA G-4.4, *Oxygen Pipeline and Piping Systems*, Compressed Gas Association, latest edition.
2. ASTM G88, *Standard Guide for Designing Systems for Oxygen Service*, American Society for Testing and Materials, West Conshohocken, PA.
3. ASTM G93, *Standard Practice for Cleaning Methods and Cleanliness Levels for Material and Equipment Used in Oxygen-enriched Environments*, American Society for Testing and Materials, West Conshohocken, PA.
4. CGA G-4.1, *Cleaning of Equipment for Oxygen Service*, Compressed Gas Association, latest edition.
5. NFPA 53M, *Fire Hazards in Oxygen-enriched Atmospheres*.
6. ASTM MNL36, *Safe Use of Oxygen and Oxygen Systems: Handbook for Design, Operation, and Maintenance*, Second Edition, H.D. Beeson, S.R. Smith, and W.F. Stewart, Editors, 2007.
7. ASTM G94, *Standard Guide for Evaluating Metals for Oxygen Service*, American Society for Testing and Materials, West Conshohocken, PA.



Figure 3-32-1—Thermal combustor on the front end of a reaction furnace on a SRU.



Figure 3-32-2—Same as figure above after damage due to oxygen combustion resulting from oxygen injection into the thermal combustor on the front end of the reaction furnace.



Figure 3-32-3—Same as figure above when viewed from a different angle.



Figure 3-32-4—Photograph of a burned 304 SS elbow. The fire started in an upstream stainless steel wire filter (due to particle impact), and the burning filter material impacted the elbow and ignited it. Thin stainless steel components (e.g. filter) are much more flammable than thicker stainless steel. Thin stainless steel ($<1/8$ in.) is usually avoided in oxygen systems.

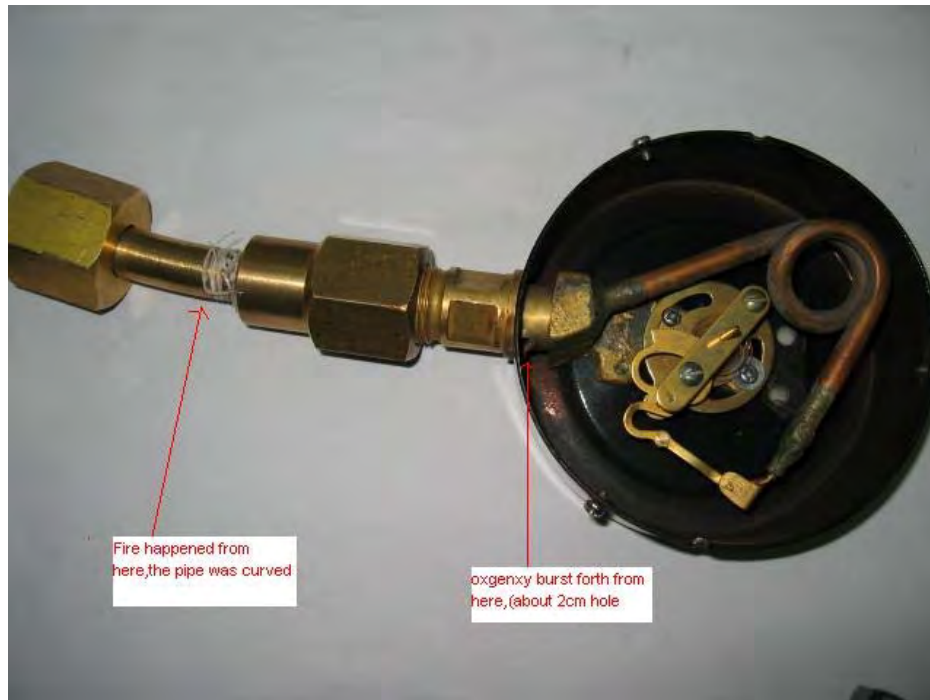


Figure 3-32-5—Photograph illustrating burn-through of a brass pressure gage. Brass is generally suitable for oxygen service. However, the gauge was not intended for oxygen service and was not “oil free.” Hydrocarbon contamination, probably from manufacture, caused the fire.

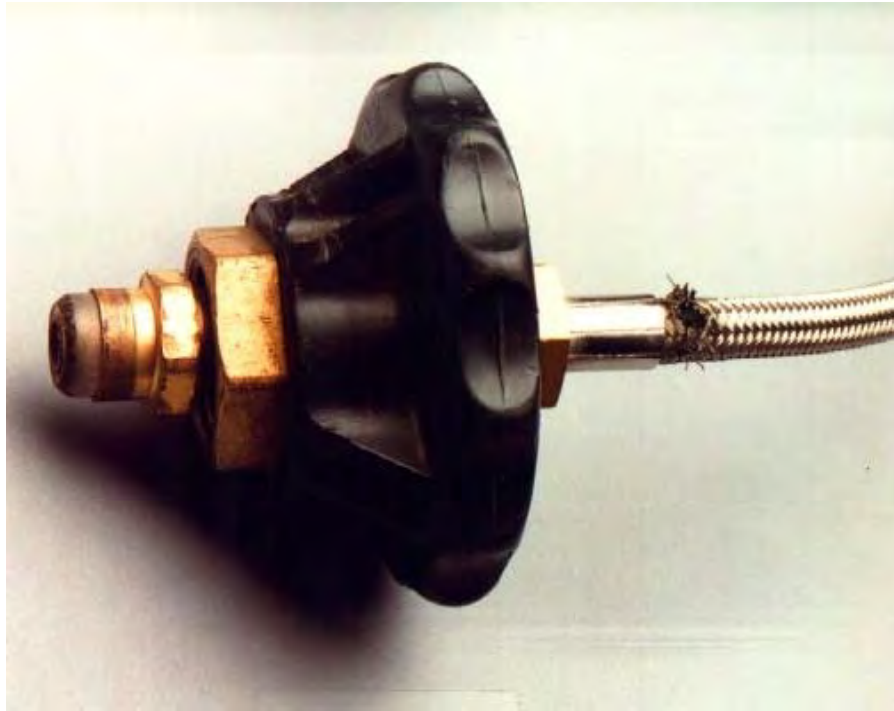


Figure 3-32-6—Burn-through of a PTFE-lined stainless steel hose in high-pressure gaseous oxygen service. Grease contamination ignited and penetrated the hose.

3.33 Graphitic Corrosion of Cast Irons

3.33.1 Description of Damage

- a) Cast irons are comprised primarily of graphite particles embedded in an iron matrix. Graphitic corrosion is a form of dealloying in which the iron matrix is corroded, leaving behind corrosion products and porous graphite.
- b) Attack results in a porous structure with a loss of strength, ductility, and density. It usually occurs under low-pH and stagnant conditions, especially in contact with soils or waters high in sulfates.

3.33.2 Affected Materials

Primarily gray cast iron, but also nodular (ductile) and malleable cast irons experience graphitic corrosion. Nodular and malleable cast irons tend to crumble when attacked. White iron is not subject to this damage because there is no free graphite.

3.33.3 Critical Factors

- a) Graphitic corrosion is usually limited to very specific microstructure-environment combinations. Factors that influence graphitic corrosion include the composition of the cast iron and exposure conditions, including temperature, degree of aeration, pH, and exposure time. Damage increases with increasing temperature and aeration, and reduced pH.
- b) Damage occurs in the presence of moisture or an aqueous phase, usually below 200 °F (95 °C).
- c) Damage may take many months or years to progress but can increase in severity if the pH drops. Much of the damage occurs during stagnant conditions when high concentrations of sulfates are present.
- d) Graphite is cathodic to the iron matrix. The iron matrix preferentially corrodes and cathodically protects the graphite in certain conductive waters or soils.
- e) Graphitic corrosion may accelerate corrosion of adjacent components by causing galvanic corrosion.

3.33.4 Affected Units or Equipment

Graphitic corrosion can occur in soft water, saltwater, mine waters, dilute acids, and in underground piping as well as in BFW equipment. Typical examples include feedwater piping, pumps [including pump impellers ([Figure 3-33-1](#) and [Figure 3-33-2](#))], valves, and underground cast iron pipe ([Figure 3-33-3](#) and [Figure 3-33-4](#)). Fire-water systems are particularly vulnerable.

3.33.5 Appearance or Morphology of Damage

- a) Graphitic corrosion normally turns cast iron charcoal gray. ([Figure 3-33-2](#) and [Figure 3-33-5](#))
- b) Damage may be widespread, or it may also occur in localized areas in which the majority of the component is unaffected.
- c) The damage may not be noticeable upon VT even where the full wall thickness is degraded.
- d) Damaged areas will be soft and easily cut or gouged with a knife or hand tool.

3.33.6 Prevention/Mitigation

- a) It is often difficult to predict if exposure conditions will cause this form of dealloying in a particular environment or service. One must be aware of the potential susceptibility of cast irons.
- b) Internal graphitic corrosion can be prevented by coatings and/or cement linings.
- c) External graphitic corrosion can be prevented by external coatings or cathodic protection in severely corrosive soils.

- d) If practical, a material other than cast iron could be substituted.

3.33.7 Inspection and Monitoring

- a) VT can be misleading as the metal surface will likely appear to be fine, other than some general surface corrosion or discoloration. VT cannot be used alone as a method of determining the presence of graphitic corrosion.
- b) Affected surface areas are soft and can be carved away with a knife, course file, screwdriver, pencil, etc. However, this is not a definitive test and can only confirm the suspect area needs further investigation.
- c) UT is not a good method to be used alone for detecting damage, but it has been reported to be able to locate the interface between sound metal and corroded metal.
- d) Acoustic techniques (loss of “metallic ring”) and ultrasonic attenuation may be applicable but are dependent upon the NDE technician’s skill and equipment.
- e) A significant reduction in hardness may accompany graphitic corrosion, although affected areas may be localized. Field hardness testing can separate sound metal from damaged areas and define the extent of the damaged area if it is not otherwise apparent.
 - 1. It may not be possible to get an actual hardness reading on severely damaged material. Rather, the brittle graphite might crack or crumble when attempting to test it. But this will clearly show that the material is affected.
- f) Core sampling in thicker sections can be utilized to help gage the depth and occurrence.
- g) Hammer testing (tapping) has been performed historically to determine the depth and extent of attack, but care must be taken because cast iron itself is brittle, and severely compromised material may fail completely. Also, hammer testing is inherently subjective.
- h) Metallographic examination may be required to confirm the extent of damage. ([Figure 3-33-6](#) to [Figure 3-33-8](#))

3.33.8 Related Mechanisms

Dealloying ([3.24](#)). Graphitic corrosion is also known as selective leaching. It should not be confused with graphitization ([3.34](#)), the decomposition of carbides in steel at high temperatures.

3.33.9 References

1. R.D. Port and H.M. Herro, *The Nalco Guide to Boiler Failure Analysis*, McGraw-Hill, New York, NY, 1991, pp. 259–263.
2. *ASM Handbook—Failure Analysis and Prevention*, Volume 11, ASM International, Materials Park, OH.
3. *ASM Handbook—Corrosion*, Volume 13, ASM International, Materials Park, OH.
4. *ASM Specialty Handbook—Cast Irons*, ASM International, Materials Park, OH, 1996.
5. M. Zamanzadeh, G. Kirkwood, S. Scheinman, and G. Bayer, “Corrosion Sensors for Detecting Graphitization of Cast Iron in Water Mains,” Paper No. 07380, *Corrosion/2007*, NACE International, Houston, TX.



Figure 3-33-1—Graphitic corrosion of a cast iron pump impeller due to glycol acidification.



Figure 3-33-2—Cutaway of the cast iron impeller shown in Figure 3-32-1. The dark phase around the outside perimeter (at arrows) is graphite that surrounds the unaffected metal in the middle.



Figure 3-33-3—View of the outside of an underground concrete-lined saltwater service line that failed from graphitic corrosion.



Figure 3-33-4—View of concrete lining inside the failed line shown in Figure 3-32-3.

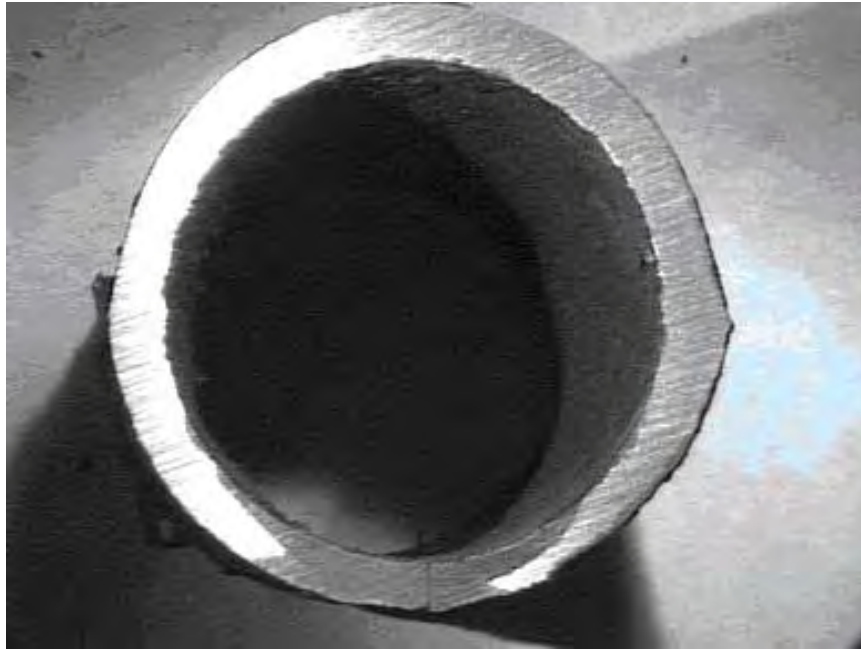


Figure 3-33-5—Cross section of a gray cast iron drainpipe showing charcoal colored thru-wall graphitic corrosion encroaching from both sides. Note the thru-wall crack at the bottom.

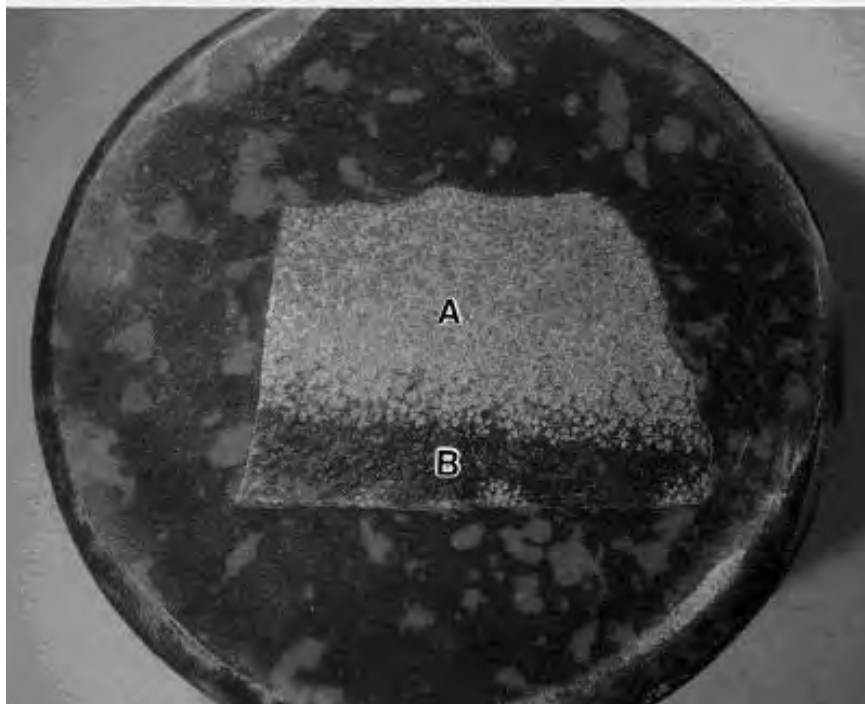


Figure 3-33-6—Cross section of a gray cast iron pipe with graphitic corrosion coming from the OD (Point B).

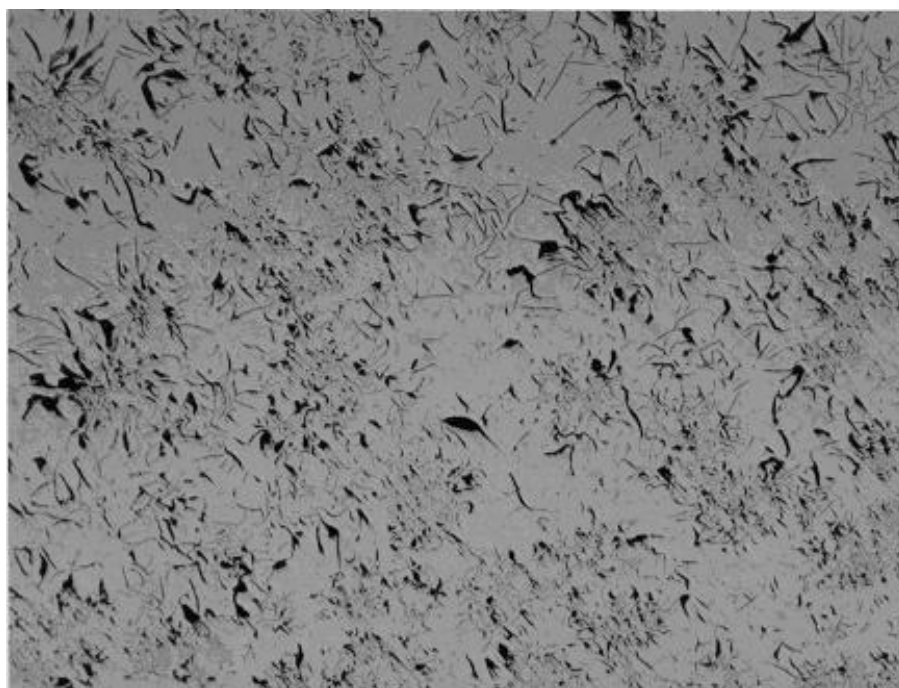


Figure 3-33-7—Higher-magnification view of unaffected area “A” shown in Figure 3-32-6.



Figure 3-33-8—Higher-magnification view of the damaged area “B” in Figure 3-32-6.

3.34 Graphitization

3.34.1 Description of Damage

Graphitization is a change in the microstructure of certain carbon steels and $\frac{1}{2}$ Mo steels after long-term operation in the 800 °F to 1100 °F (425 °C to 595 °C) range. At these temperatures, the carbide phases in these steels are unstable and decompose into graphite nodules. This decomposition of carbides may cause a loss in strength, ductility, and/or creep resistance.

3.34.2 Affected Materials

Some grades of carbon steel and $\frac{1}{2}$ Mo steels.

3.34.3 Critical Factors

- a) The most important factors that affect graphitization are the chemical composition of the steel, stress, temperature, and time of exposure.
- b) Graphitization is not commonly observed. Some steels are much more susceptible to graphitization than others, but exactly what causes some steels to graphitize while others are resistant is not well understood. It was originally thought that silicon and aluminum content played a major role, but it has been shown that they have negligible influence on graphitization.
- c) Graphitization has been found in low-alloy C-Mo steels with up to 1 % Mo. The addition of about 0.7 % chromium has been found to eliminate graphitization.
- d) Temperature has an important effect on the rate of graphitization. Below 800 °F (425 °C), the rate is extremely slow. The rate increases with increasing temperature.
- e) There are two general types of graphitization.
 1. First is random graphitization in which the graphite nodules are distributed randomly throughout the steel. While this type of graphitization may lower the room-temperature tensile strength, it does not usually lower the creep resistance.
 2. The second and more damaging type of graphitization results in chains or local planes of concentrated graphite nodules. Because of its appearance, this type is also known as "eyebrow graphitization." This form of graphitization can result in a significant reduction in load-bearing capability while increasing the potential for brittle fracture along this plane. There are two forms of this type of graphitization: (1) weld HAZ graphitization and (2) non-weld graphitization.
 - Weld HAZ graphitization is found adjacent to welds in a narrow band along the low-temperature edge of the HAZ. In multi-pass welded butt joints, these zones overlap each other. The graphite nodules that form at the low-temperature edge of these HAZs create a band of weak graphite extending through the entire cross section. (Figure 3-34-1 and Figure 3-34-2)
 - Non-weld graphitization is a form of localized graphitization that sometimes occurs along grain boundaries, constituent boundaries (between ferrite and pearlite), or planes of localized yielding in steels that have experienced significant plastic deformation as the result of cold working operations or bending. This type of graphitization also occurs in a chain-like manner.
- f) The extent and degree of graphitization is usually reported in a qualitative fashion (none, slight, moderate, severe). Although it is difficult to predict the rate at which it forms, severe HAZ graphitization can develop in as little as 5 years at service temperatures above 1000 °F (540 °C). Very slight graphitization would be expected to be found after 30 to 40 years at 850 °F (455 °C). Time-temperature-transformation curves for HAZ graphitization can be found in Reference 2.

3.34.4 Affected Units or Equipment

- a) Graphitization primarily occurs in carbon steel piping and hot-wall equipment in the FCC, catalytic reforming, and coker units.
- b) Bainitic grades are less susceptible than coarse pearlitic grades.
- c) Few failures directly attributable to graphitization have been reported in the refining industry. However, graphitization has been found where failure resulted primarily from other causes.
- d) Several serious cases of graphitization have occurred in the reactors and piping of FCC units, as well as in carbon steel furnace tubes in a thermal cracking unit. Graphitization led to the failure of seal welds at the bottom tubesheet of a vertical waste heat boiler in an FCC. A graphitization failure was also reported in the long seam weld of a C-1/2Mo catalytic reformer reactor/interheater line.
- e) Where concentrated eyebrow graphitization occurs along HAZs, the creep rupture strength may be drastically lowered. Slight to moderate amounts of graphite along the HAZs do not appear to significantly lower room-temperature or high-temperature properties.
- f) Graphitization seldom occurs on boiling surface tubing in boilers but did occur in low-alloy C-1/2Mo tubes and headers during the 1940s. Economizer tubing, steam piping, and other related equipment that operates in the temperature range of 850 °F to 1025 °F (440 °C to 550 °C) are more likely to suffer graphitization.

3.34.5 Appearance or Morphology of Damage

- a) Graphitization is not visible or readily apparent and can only be observed by metallographic examination. ([Figure 3-34-2](#) to [Figure 3-34-4](#))
- b) At an advanced stage resulting in loss of creep strength, microvoids, microfissuring, subsurface cracking, or surface-connected cracking may be found.

3.34.6 Prevention/Mitigation

Graphitization can be prevented by using chromium containing low-alloy steels for long-term operation above 800 °F (425 °C).

3.34.7 Inspection and Monitoring

- a) Evidence of graphitization is most effectively evaluated through removal of full-thickness samples for examination using metallographic techniques. Damage may occur mid-wall so that field replicas may be inadequate. Samples should be taken from areas where maximum temperature limits have been exceeded
- b) Advanced stages of damage related to loss in strength include surface-breaking cracks or creep deformation that may be difficult to detect.

3.34.8 Related Mechanisms

Spheroidization ([3.59](#)) and graphitization are competing mechanisms that occur at overlapping temperature ranges. Spheroidization tends to occur preferentially above 1025 °F (550 °C), while graphitization predominates below this temperature.

3.34.9 References

1. H. Thielsch, *Defects and Failures in Pressure Vessels and Piping*, Rheinhold Publishing, New York, NY, 1965, pp. 49–83.

2. J.R. Foulds and R. Viswanathan, "Graphitization of Steels in Elevated-temperature Service," *Proceedings of the First International Symposium: Microstructures and Mechanical Properties of Aging Materials*, November 1992.
3. R.D. Port, "Non-weld-related Graphitization Failures," Paper No. 89248, *Corrosion/89*, NACE International, Houston, TX.
4. *ASM Handbook—Properties and Selection: Iron, Steels, and High-performance Alloys*, Volume 1, ASM International, Materials Park, OH.
5. D.N. French, "Microstructural Degradation," The National Board of Boiler and Pressure Vessel Inspectors, <http://www.nationalboard.com>, June 2001.
6. J.G. Wilson, *Part 1: Graphitization of Steel in Petroleum Refining Equipment*, WRC Bulletin 032, Shaker Heights, OH, January 1957.
7. J.D. Dobis and L. Huang, "Assessment of Graphitized Carbon Steel Tubes in Fired Heater Service," Paper No. 05559, *Corrosion/2005*, NACE International, Houston, TX.
8. *Review of the Existing Technology for the Detection of Graphitization Damage in Carbon and Carbon-Molybdenum Steel Piping and Tubing*, EPRI, Product ID: 3002003421, July 2, 2014.
9. H.J. Kerr and F. Eberle, "Graphitization of Low-carbon and Low-carbon-molybdenum Steels," *Welding Research Supplement*, February 1945.
10. J. Hau et al., "Evaluation of Aging Equipment for Continued Service," Paper No. 05558, *Corrosion/2005*, NACE International, Houston, TX.



Figure 3-34-1—A crack opened up along the low-temperature edge of the HAZ when a graphitized piece of steel was subjected to a bending test. The scale in the photo is in tenths of an inch. (Reference 10)

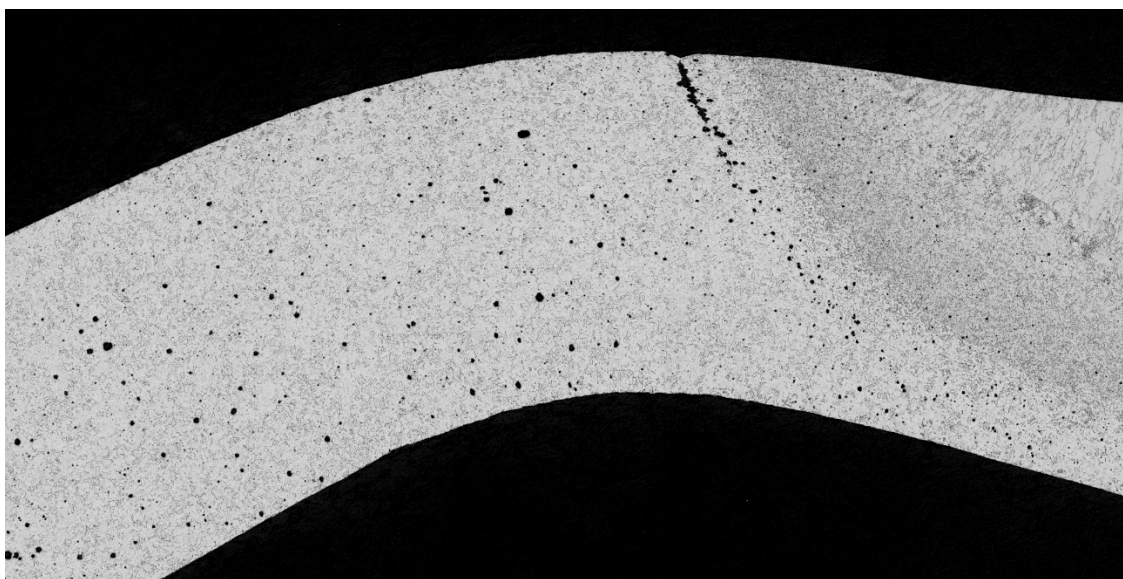


Figure 3-34-2—A polished and etched side view of the sample in Figure 3-33-1 shows aligned graphitization along the low-temperature edge of the HAZ as well as random graphitization in the base metal. (Reference 10)

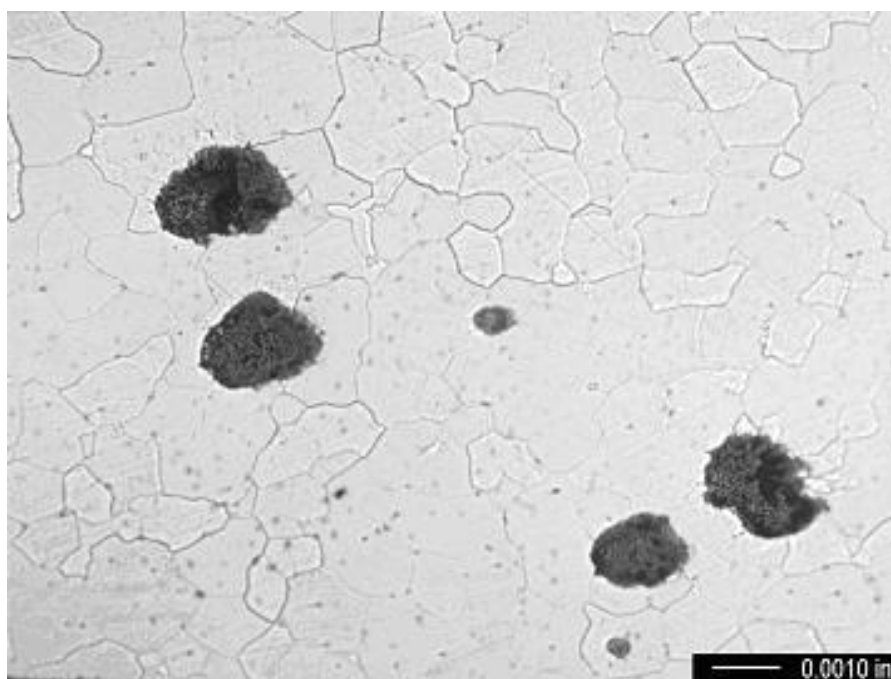


Figure 3-34-3—High-magnification photomicrograph of a metallographic sample showing graphite nodules. Compare to normal microstructure shown in Figure 3-33-4.

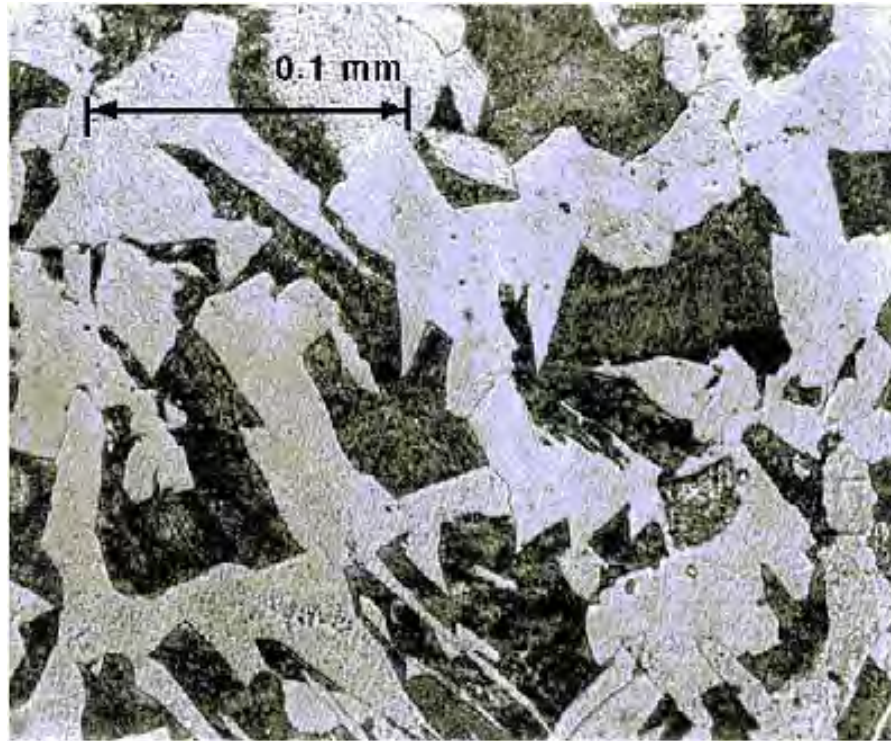


Figure 3-34-4—High-magnification photomicrograph of metallographic sample showing typical ferrite-pearlite structure of carbon steel.

3.35 High-temperature H₂/H₂S Corrosion

3.35.1 Description of Damage

The presence of hydrogen in H₂S-containing hydrocarbon streams increases the severity of high-temperature sulfidation (sulfidic) corrosion at temperatures above about 450 °F (230 °C). Because of the smooth, large, relatively uniformly corroded surface produced by high-temperature H₂/H₂S corrosion, it can lead to rupture-type failure rather than a localized or pinhole leak. This subject is covered in much greater detail in Reference 3 (API 939-C).

3.35.2 Affected Materials

For the materials typically used in this service, the order of increasing resistance is carbon steel, low-alloy steels, 400 series SS, and 300 series SS. However, for a practical, useful improvement over carbon steel, the alloy content of at least 9Cr-1Mo is normally needed.

3.35.3 Critical Factors

- The critical factors for high-temperature H₂/H₂S corrosion are the temperature, the presence of hydrogen, the concentration and partial pressure of H₂S, the vapor/liquid ratio, and the chemical composition of the alloy.
- Depending on the quantity of hydrogen present, corrosion rates may be significantly different than those associated with high-temperature sulfidation in the absence of hydrogen. (See [3.61](#).)
- Sulfidation rates increase with increasing H₂S content and especially increasing temperature. [Figure 3-35-1](#) shows the effect of temperature and H₂S content on the corrosion rate of carbon steel.
- Increasing chromium content of the alloy improves resistance. However, there is little improvement with increasing chromium content until about 7 % to 9 % Cr as shown by the relative rate reduction factors in [Table 3-35-1](#). The benefit of higher chromium levels is shown in [Figure 3-35-2](#).
- Chromium-containing nickel-based alloys have resistance similar to stainless steel. Similar levels of chromium provide similar corrosion resistance.
- Primarily due to the higher partial pressure of H₂S, corrosion rates in higher-pressure units, e.g. hydrocrackers and gas oil hydrotreaters (desulfurizers), are generally higher than those in lower-pressure naphtha hydrotreaters.

3.35.4 Affected Units or Equipment

- This form of corrosion occurs in piping and equipment in units where high-temperature H₂/H₂S streams are found, which is primarily hydroprocessing units (hydrotreaters and hydrocrackers).
- Noticeable increases in corrosion rates may be found downstream of the hydrogen injection point where the mechanism changes from sulfidation ([3.61](#)) to high-temperature H₂/H₂S corrosion. The addition of hydrogen promotes cracking of the reactive sulfur species into H₂S prior to the reactor, increasing the rate of corrosion in comparison to corrosion from the reactive sulfur alone.

3.35.5 Appearance or Morphology of Damage

- Corrosion will appear as a uniform loss in thickness from the process side and is accompanied by the formation of an iron sulfide scale.
- Scale is about five times the volume of lost metal and may be in multiple layers.
- The tightly adherent shiny gray scale attached to the surface may be mistaken for unaffected metal.

3.35.6 Prevention/Mitigation

- a) The corrosion damage is minimized by using alloys with sufficiently high chromium content.
- b) The 300 series SS such as Types 304L, 316L, 321, and 347 are highly resistant at typical service temperatures.
- c) Aluminum diffusion treatment is sometimes used to reduce corrosion rates and prolong the life of thin components such as 300 series SS catalyst support screens in hydroprocessing reactors.
- d) Process simulations should be checked periodically to confirm that H₂S levels have not significantly increased.

3.35.7 Inspection and Monitoring

- a) Thinning in piping and tubing can be detected and measured using UT thickness measurement or RT. Thinning in pressure vessels can be detected by internal VT and measured with UT.
- b) Permanently mounted thickness monitoring sensors can be used.
- c) Thinning in heater tubes can be detected using UT or by smart pigging. Smart pigging provides a more thorough examination and may find thinning missed by spot UT testing.
- d) Actual operating temperatures should be verified and compared against design. Temperatures and sulfur levels should be monitored for increases above design.
- e) Temperatures can be monitored using tube-skin thermocouples and/or infrared thermography.

3.35.8 Related Mechanisms

High-temperature sulfidation in the absence of hydrogen is discussed in [3.61](#).

3.35.9 References

1. J. Gutzeit, R.D. Merrick, and L.R. Scharfstein, "Corrosion in Petroleum Refining and Petrochemical Operations," *Metals Handbook*, Volume 13, ASM International, Materials Park, OH, 1987, pp. 1262–1287.
2. *Corrosion Control in the Refining Industry*, NACE Course Book, NACE International, Houston, TX, 1999.
3. API Recommended Practice 939-C, *Guidelines for Avoiding Sulfidation (Sulfidic) Corrosion Failures in Oil Refineries*, American Petroleum Institute, Washington, DC.

Table 3-35-1—Rate Factors vs Chromium Content (Reference 2)

Alloy	Rate Factor
CS, C-0.5Mo	1
1Cr-0.5Mo	0.96
2.25Cr-1Mo	0.91
5Cr-0.5Mo	0.80
7Cr-1Mo	0.74
9Cr-1Mo	0.68

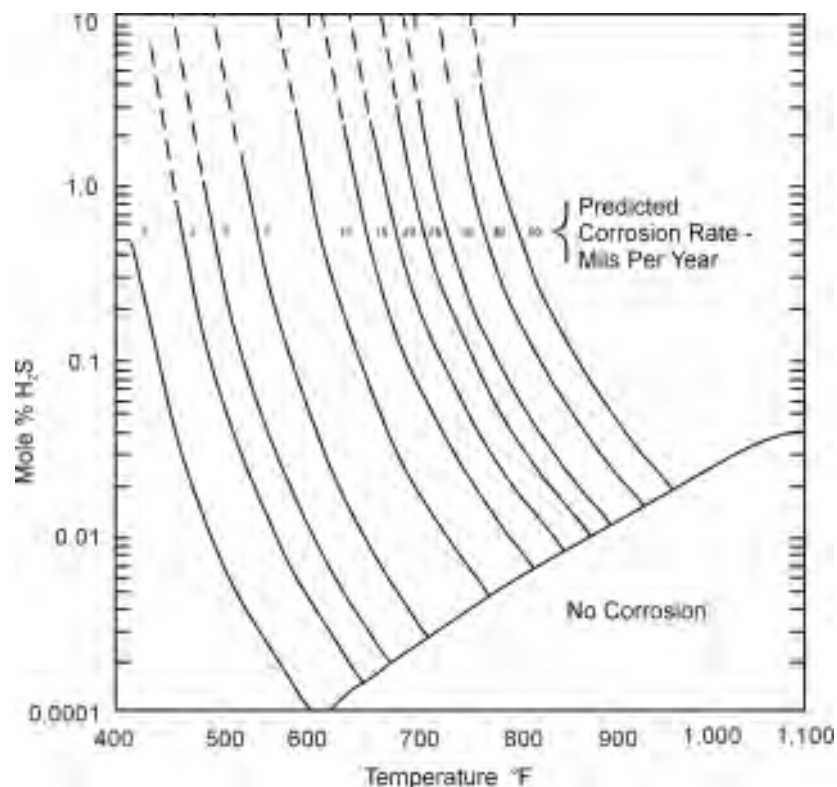


Figure 3-35-1—Corrosion rate of carbon steel in H_2/H_2S service in a naphtha desulfurizer from the modified Couper-Gorman curves. (Reference 1)

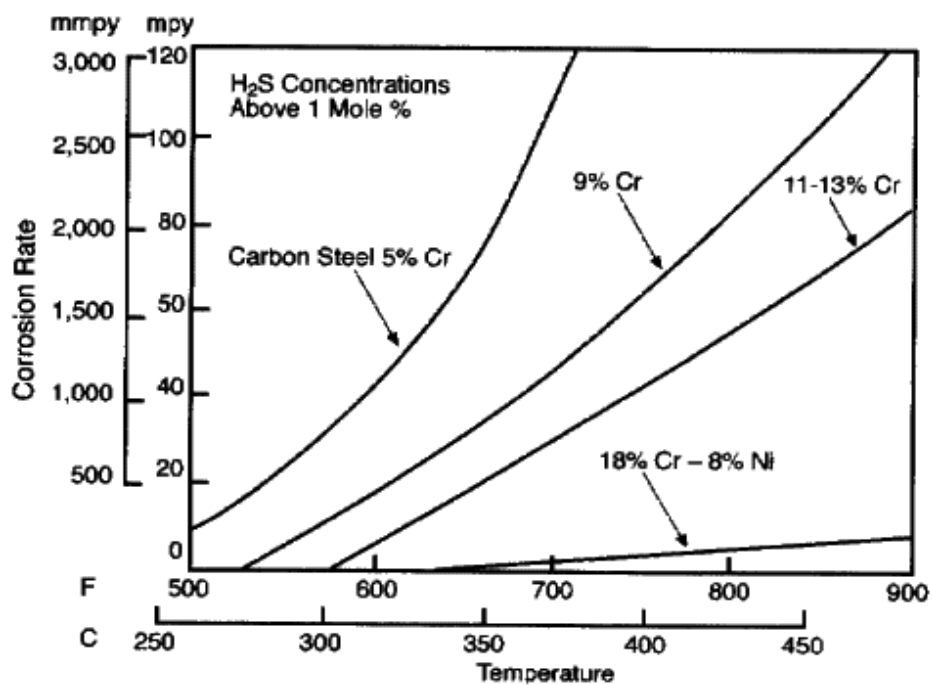


Figure 3-35-2—Corrosion rate curves for Cr-containing alloys in H_2/H_2S service. (Reference 1)

3.36 High-temperature Hydrogen Attack

3.36.1 Description of Damage

- a) High-temperature hydrogen attack (HTHA) results from exposure of steels to hydrogen gas at elevated temperatures and pressures. Dissociated hydrogen atoms react with carbon and carbides in the steel to form CH_4 .
- b) The hydrogen/carbon reaction can cause surface decarburization of the steel. Surface decarburization alone is normally not detrimental to the point of limiting the life of equipment but may be indicative of internal HTHA. Extensive decarburization will reduce component strength. (See 3.25 for more on decarburization.)
- c) If diffusion of carbon to the surface is limited, CH_4 is formed internally from internal decarburization. Internal CH_4 cannot diffuse through the steel. As a result, internal CH_4 pressure builds up, initially forming bubbles or cavities, then microfissures, and finally fissures that may combine to form cracks. Internal damage leading to cracking is the more serious effect of HTHA, and it can lead to equipment failure.
- d) Failure can occur when the cracks reduce the load (pressure) carrying ability of the pressure-containing part.
- e) Blistering may also occur due to either molecular hydrogen (from re-combined hydrogen atoms) or CH_4 accumulating in laminations or other conducive sites in the steel.
- f) See Reference 1 (API RP 941) for more detailed information on HTHA.

3.36.2 Affected Materials

- a) In order of increasing resistance: as-welded (non-PWHT) carbon steel, non-welded carbon steel and carbon steel that has received PWHT, C-0.5Mo, Mn-0.5Mo, 1Cr-0.5Mo, 1.25Cr-0.5Mo, 2.25Cr-1Mo, 2.25Cr-1Mo-V, 3Cr-1Mo, 5Cr-0.5Mo, and similar steels with variations in chemistry.
- b) 300 series SS, as well as 5Cr, 9Cr, and 12Cr alloys, are not susceptible to HTHA at conditions normally seen in refinery units.

3.36.3 Critical Factors

- a) Resistance to HTHA increases with an increase in the alloy content, primarily the Cr and Mo content, of a steel. For a specific material, HTHA is dependent on temperature, hydrogen partial pressure, time, and stress level.
- b) Figure 3-36-1, from API RP 941, is a set of curves that show the combined temperature and hydrogen partial pressure safe operating limits for carbon steel and low-alloy steels. Operation at a temperature and H_2 partial pressure below the curve for a particular material is considered safe. Operation above the curve indicates susceptibility to HTHA. Additional information on HTHA can be found in API RP 941.
- c) HTHA damage is preceded by a period of time when no noticeable change in properties is detectable by normal mechanical testing techniques nor is any internal damage detectable with any NDE methods. This period of time is called the incubation period.
 - 1. During the incubation period, the amount of internal damage (cavity and microfissure formation and growth) increases to the point where it can be detected and measured with available inspection techniques. It may vary from hours under very severe conditions to many years.
- d) The damage is irreversible, and service exposure time is cumulative. After the incubation period, the amount of damage continues to increase during the time the material is exposed to damaging temperature and H_2 partial pressure conditions, whether the exposure is continuous or periodic.
- e) Applied or residual tensile stress can increase the rate of HTHA damage occurring in a susceptible material. Stress-relieving carbon steel welds by PWHT is known to reduce susceptibility to HTHA.

3.36.4 Affected Units

- a) Hydroprocessing units such as hydrotreaters (desulfurizers) and hydrocrackers, catalytic reformers, some ISOM units, hydrogen manufacturing units, and hydrogen cleanup units such as pressure swing absorption units all have equipment operating under conditions where HTHA can occur in a susceptible material.
- b) Boiler tubes in very high pressure steam service can also suffer HTHA.

3.36.5 Appearance or Morphology of Damage

- a) The location within a piece of equipment where HTHA will occur is generally unpredictable. HTHA that led to equipment failure or replacement has occurred in weld HAZs as well as base metal away from welds. It is less commonly found in weld metal.
- b) HTHA can be confirmed through the use of specialized techniques including metallographic and SEM analysis of damaged areas. (Figure 3-36-2 to Figure 3-36-6)
- c) The steel surface may be decarburized. (Figure 3-36-4)
- d) Internal decarburization can lead to internal fissuring and cracking, which in the later stages of damage can be seen using standard metallography. (Figure 3-36-5 to Figure 3-36-6)
- e) In the earliest stages of HTHA, bubbles/cavities in samples can be detected by SEM, although it may be difficult to tell the difference between HTHA cavities and creep cavities. (Some refinery services expose low-alloy steels to both HTHA and creep conditions.) Advanced metallographic analysis of damaged areas can detect the early stages of microfissuring.
- f) Cracking and fissuring are intergranular and occur adjacent to pearlite (layers of ferrite and iron carbide) areas in carbon steels.
- g) Cracking along the HAZ and fusion line can occur in carbon steel as the result of highly localized HTHA, with adjacent areas exhibiting little or no fissuring or decarburization
- h) Blistering may be visible to the naked eye.

3.36.6 Prevention/Mitigation

- a) Using alloy steels with chromium and molybdenum will increase carbide stability, thereby minimizing CH₄ formation and resistance to HTHA. Other carbide stabilizing elements include tungsten and vanadium.
- b) Common design practice is to use a 25 °F to 50 °F (15 °C to 30 °C) and 25 psia to 50 psia (170 KPa to 345 KPa) hydrogen partial pressure safety factor approach when using the API RP 941 curves.
- c) The API RP 941 curves, with the current version shown in Figure 3-36-1, have been revised several times since they were first introduced.
 - 1. The C-½Mo curve was removed from Figure 3-36-1 in 1990 because of a number of cases of HTHA in C-½Mo steels in refinery service under conditions that were previously considered safe, i.e. below the previously existing C-½Mo curve. This material is not recommended for new construction in hot hydrogen services. (C-½Mo carbide stability under HTHA conditions is variable due to the different carbides formed during the various heat treatments applied to fabricated equipment.)
- d) For existing C-½Mo equipment, the concern about its unpredictable resistance to HTHA has prompted refiners to perform reviews of inspection effectiveness and cost vs replacement with a more suitable alloy.
 - 1. Non-stress-relieved carbon steel welds have also shown a higher susceptibility to HTHA compared to stress-relieved welds and non-welded components. In response, the Eighth Edition of API RP 941 added a new, lower curve for carbon steel welded with no PWHT, as shown in Figure 3-36-1.

- e) 300 series SS weld overlay and roll bond cladding, and in some cases 400 series SS cladding, are typically used in high-temperature hydrogen service where the base metal does not have adequate high-temperature H_2/H_2S corrosion resistance. Properly metallurgically bonded stainless steel overlay or cladding will decrease the hydrogen partial pressure seen by the underlying base metal; however, most refiners do not take credit for this in the design of new equipment. New equipment should be designed so the base material is inherently resistant to HTHA under expected service conditions without taking into account any added HTHA resistance provided by the weld overlay or cladding.
 - 1. In some cases, refiners take the decrease in effective partial pressure into account when evaluating the risk of HTHA in existing equipment.

3.36.7 Inspection and Monitoring

- a) Damage may occur randomly in the base metal, weld HAZs, and occasionally in welds.
- b) HTHA can occur in the base metal at locations remote from welds. In vessels with internal cladding or weld overlay, HTHA damage can occur in the base metal at locations where the cladding or weld overlay has cracked and become disbonded, especially if credit was taken for the cladding reducing the effective H_2 partial pressure at the base metal, i.e. where the vessel's operating conditions exceeded the API RP 941 curve for unprotected base metal. PT of the cladding or weld overlay for cracking can assist in identifying areas that may have HTHA damage in the base metal underneath the cracked cladding or weld overlay.
 - 1. VT for bulging of the cladding or weld overlay away from the underlying base metal may also aid in identifying suspect areas of HTHA damage in the base metal.
 - 2. Localized damage under cladding or weld overlay might be overlooked if inspection methods focus only on the weld seams and nozzles. (Reference 4)
- c) While FMR can detect microvoids, fissures, and decarburization, it is best suited for examination in areas of known HTHA damage and is generally not relied upon as the primary tool for damage detection. Most equipment has decarburized surfaces due to the various heat treatments used during fabrication, and microvoids and fissures may also be absent on the surface. Experience has shown that removal of metal up to 0.1 in. (2 mm) may be needed for finding HTHA damage.
- d) VT for blisters on the inside surface may indicate CH_4 formation and potential HTHA. However, HTHA mostly occurs without the formation of surface blisters.
- e) The use of NDE methods to detect internal HTHA requires highly specialized training, skills, and experience. It has had mixed results and is an area of ongoing development. As of this writing, the NDE table in API RP 941 is undergoing revision.
 - 1. Automated ultrasonic backscatter testing (AUBT) and angle beam spectral analysis (ABSA) have had some success finding fissuring, i.e. where microvoids and microfissures have grown to form significant fissures in the base metal as well as in welds and HAZs, but it can also miss significant cracking and is not considered reliable.
 - 2. TOFD and PAUT have shown promise in finding surface-connected and internal damage.
 - 3. Conventional NDE methods for crack detection, e.g. WFMT, PT, or MT, are generally not useful for HTHA inspection except where gross cracking has occurred and reached the metal surface.
 - 4. AET is not a proven method for the detection of damage.
 - 5. Ultrasonic attenuation and velocity ratio have been found to be unreliable techniques for HTHA detection and should not be used as primary inspection methods.

3.36.8 Related Mechanisms

Decarburization (3.25). A form of HTHA can occur in boiler tubes and is referred to by the fossil utility industry as hydrogen damage.

3.36.9 References

1. API Recommended Practice 941, *Steels for Hydrogen Service at Elevated Temperatures and Pressures in Petroleum Refineries and Petrochemical Plants*, 8th Edition, American Petroleum Institute, Washington, DC
2. F.H. Vitovec et al., "The Growth Rate of Fissures During Hydrogen Attack of Steels," *Proceedings of the API Division of Refining*, Vol. 44, No. 3, 1964, pp. 179–188.
3. "Fitness-For-Service Evaluation Procedures for Operating Pressure Vessels, Tanks, and Piping in Refinery and Chemical Service," Materials Properties Council, FS-26, Draft No. 5, Consultants Report, NY, 1995.
4. S. Decker et al., "Safe Operation of a High Temperature Hydrogen Attack Affected DHT Reactor," Paper No. 09339, *Corrosion/2009*, NACE International, Houston, TX.

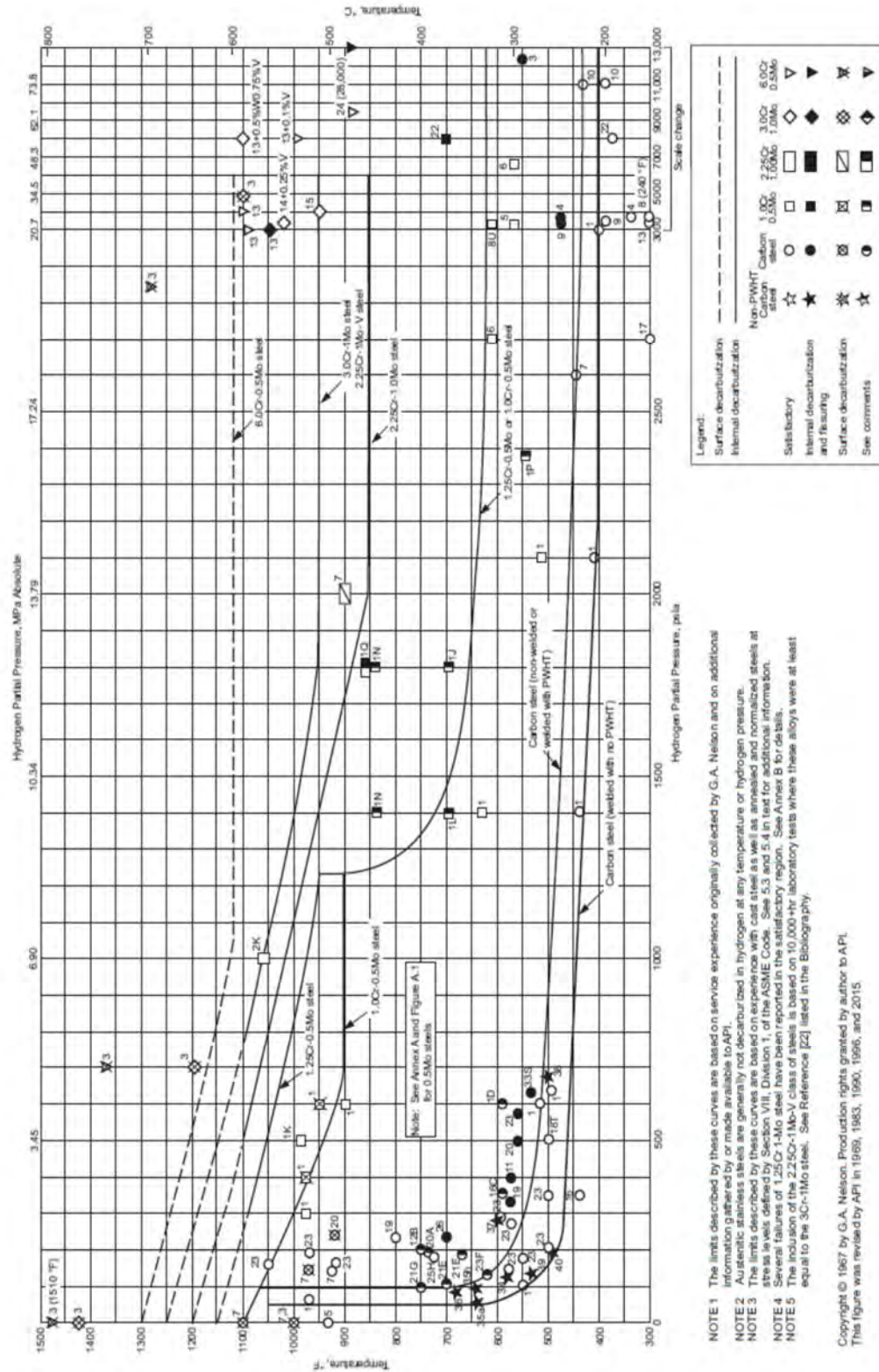


Figure 3-36-1—Recommended temperature and H₂ partial pressure limits per API RP 941. (Reference 1)



Figure 3-36-2—A pair of 10-in. C- $\frac{1}{2}$ Mo flanged pipe sections (SA335-P1 and SA234-WP1) from a hot bypass line in a catalytic reformer that was designed to remain closed but operated partially or fully open for unknown lengths of time. They were in service for ~34 years at temperatures up to 960 °F (515 °C) with a hydrogen partial pressure of 198 psig (1.4 MPa).



Figure 3-36-3—A photomicrograph of the OD surface of a pipe section from Figure 3-35-2 exhibits a normal ferritic-pearlitic microstructure. Magnification 200X.



Figure 3-36-4—A photomicrograph at the ID surface of the pipe in Figure 3-35-2 shows complete decarburization of the original structure. Magnification 200X.

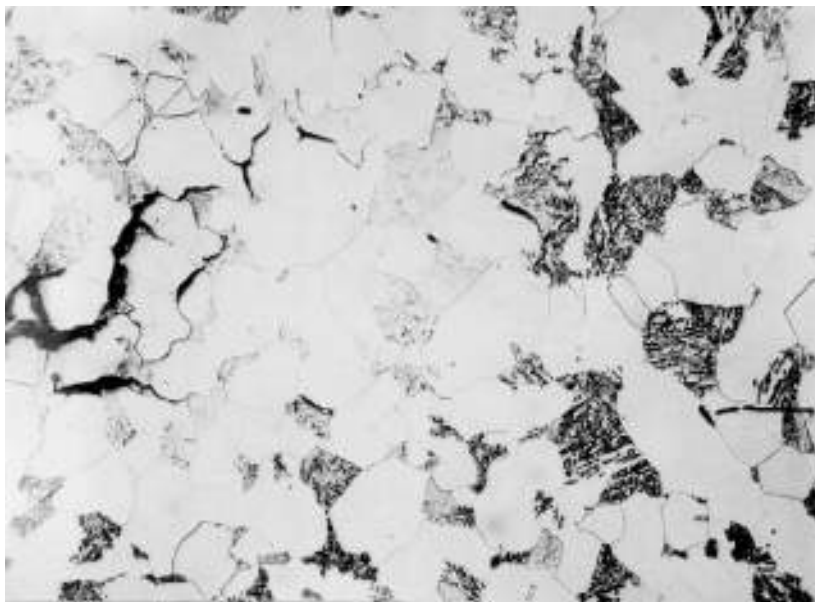


Figure 3-36-5—A photomicrograph illustrating internal decarburization and fissuring of C- $\frac{1}{2}$ Mo steel.

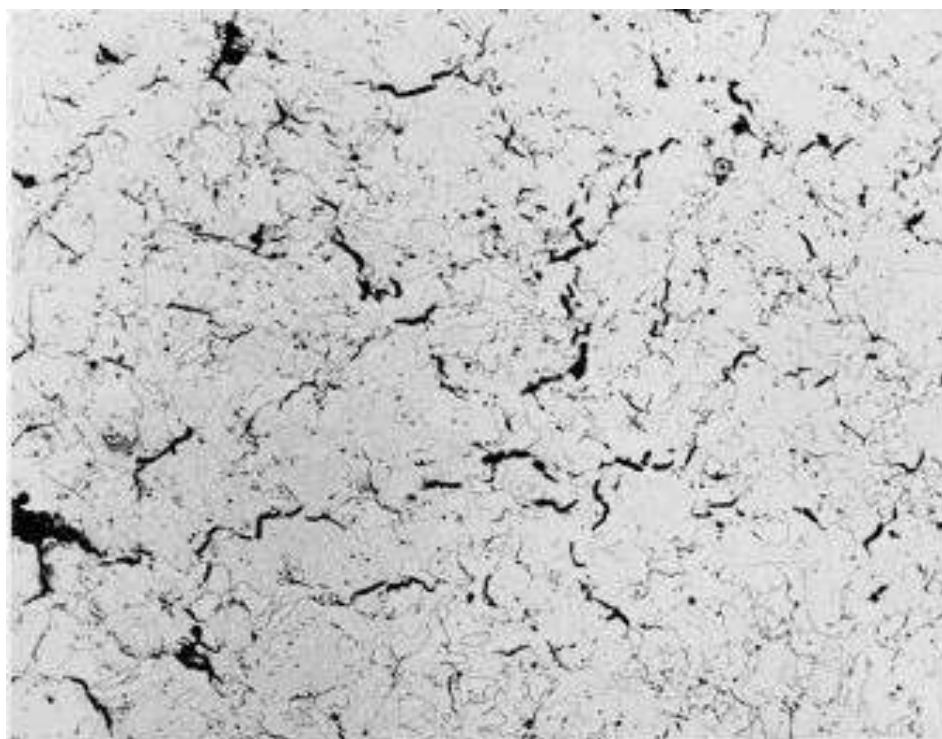


Figure 3-36-6—A high-magnification photomicrograph showing linkup of microfissures to form continuous cracks. Note that damage is accompanied by a significant amount of internal decarburization.

3.37 Hydrochloric Acid Corrosion

3.37.1 Description of Damage

- a) Hydrochloric acid (aqueous HCl) causes both general and localized corrosion and is very aggressive to most common materials of construction across a wide range of concentrations.
- b) Damage in refineries is most often associated with dew point corrosion in which vapors containing water and hydrogen chloride condense from the overhead stream of a distillation, fractionation, or stripping tower. The first water droplets that condense can be highly acidic (low pH) and promote high corrosion rates.

3.37.2 Affected Materials

All common materials of construction used in refineries.

3.37.3 Critical Factors

- a) HCl acid concentration, temperature, and alloy composition.
- b) The severity of corrosion increases with increasing HCl concentration and increasing temperature.
- c) Aqueous HCl can form beneath deposits of ammonium chloride or amine hydrochloride salts in exchangers and piping. The deposits readily absorb water from the process stream or from injected wash water. Hydrogen chloride gas is normally not corrosive in dry process streams but becomes very corrosive where water is available to form hydrochloric acid.
- d) Carbon steel and low-alloy steels are subject to excessive corrosion when exposed to any concentration of HCl acid that produces a pH below about 4.5
- e) 300 series SS and 400 series SS are not usefully resistant to HCl at any concentration or temperature.
- f) Alloy 400, titanium, and some other nickel-based alloys have good resistance to dilute HCl acid in many refinery applications.
- g) The presence of oxidizing agents (oxygen, ferric and cupric ions) will increase the corrosion rate, particularly for Alloy 400 and Alloy B-2. Titanium performs well in oxidizing conditions but fails rapidly in dry HCl service.

3.37.4 Affected Units or Equipment

HCl corrosion is found in several units, especially crude and vacuum units, hydroprocessing units, and catalytic reformer units.

- a) Crude units.
 - 1. In the atmospheric tower overhead system, corrosion from HCl acid occurs as the first droplets of water condense from the vapor stream off the top of the tower. This water can have a very low pH and can result in high rates of corrosion in piping, as well as exchanger shells, tubes and header boxes, and cold dead-legs.
 - 2. HCl corrosion can also be a problem in the vacuum ejector and condensing equipment off the top of the vacuum tower.
- b) Hydroprocessing units.
 - 1. Chlorides may enter the unit as inorganic or organic chloride in the hydrocarbon feed, or with the recycle hydrogen, and react to form HCl.

2. Ammonium chloride salts can form in various parts of the unit, including the effluent side of the hot feed/effluent exchangers because both NH_3 and HCl are present and they may condense with water in the effluent train.
3. HCl -containing streams can migrate through the fractionation section, resulting in severe acid dew point corrosion at the mixing point where the stream contacts water.

c) Catalytic reforming units.

1. Chlorides may be stripped from the catalyst and react to form HCl that carries through the effluent train, regeneration system, stabilizer tower, debutanizer tower, and feed/preheat exchangers.
2. HCl -containing vapors can migrate through the gas plant fractionation section, resulting in corrosion at mix points where HCl -containing vapor streams mix with streams containing free water. HCl corrosion can also occur in these streams where they cool below the acid dew point and in water boots and lines off the water boots.

3.37.5 Appearance or Morphology of Damage

- a) Carbon steel and low-alloy steels suffer uniform thinning, localized corrosion, or under-deposit attack.
- b) 300 series SS and 400 series SS will often suffer pitting attack, and 300 series SS may experience Cl^- SCC if the temperature is sufficiently high. (See 3.17.)

3.37.6 Prevention/Mitigation

a) Crude units.

1. Optimizing the crude oil tank water separation and withdrawal and crude desalting operation will help reduce chloride content in the feed to the crude tower. A common target is 20 ppm or fewer chlorides in the overhead accumulator water.
2. Upgrading carbon steel to nickel-based alloys or titanium can reduce HCl acid corrosion problems.
3. Water wash can be added to quench the overhead stream and to help dilute the condensing hydrochloric acid concentration.
4. Caustic injection downstream of the desalter is another common method used to reduce the amount of HCl going overhead. Proper design and operating guidelines should be followed to avoid caustic SCC (3.15) and fouling in the feed preheat train.
5. Various combinations of ammonia, neutralizing amines, and filming amines can be injected in the atmospheric tower overhead line before the water dew point.
6. Well-maintained process monitoring locations, e.g. for measuring chloride content, water injection rates, and chemical injection rates, are important for managing HCl corrosion.

b) Hydroprocessing.

1. Carryover of water and chloride salts, including neutralizing amine hydrochloride salts, should be minimized.
2. HCl in H_2 streams should be minimized (e.g. by installing scrubbers or guard beds to remove HCl from hydrogen produced in catalytic reforming units).
3. Corrosion-resistant nickel-based alloys should be used where necessary.
4. Well-maintained process monitoring locations are important for minimizing the effects of HCl corrosion.

c) Catalytic reforming.

1. Same as hydroprocessing, but in addition, water washing the hydrocarbon stream has also been used to remove the highly water-soluble chlorides. Special care in the design and operation of this equipment is needed. Minimizing water and/or oxygenates in the feed will reduce stripping of chlorides from the catalyst.
2. Special adsorbents in chloride beds and chloride treaters can be used to remove chlorides from the recycle hydrogen streams and from liquid hydrocarbon streams.
3. Well-maintained process monitoring locations are important for minimizing the effects of HCl corrosion.

3.37.7 Inspection and Monitoring

- a) Hydrochloric acid causes both general and localized corrosion and is very aggressive to most common materials of construction, especially carbon steel, across a wide range of concentrations.
- b) Where applicable, VT should be performed on all accessible components with the potential for hydrochloric acid corrosion. These areas of concern can be characterized by orange-yellow discoloration of the affected material with scale buildup and various levels of deterioration.
- c) UT thickness mapping, including AUT, can be utilized to determine the extent of localized thinning.
- d) RT can be utilized to find or monitor localized thinning in piping components. RT is often performed at transition components (e.g. elbows, three-way or four-way fittings, and dead-legs).
- e) Strategically placed corrosion probes and/or corrosion coupons can provide additional information on the rate and extent of damage.
- f) Permanently mounted thickness monitoring sensors can be used.
- g) The pH of the water in the boot of the atmospheric tower overhead accumulator should be checked regularly. Other variables including chloride and iron content are typically checked on a less frequent basis but do need to be monitored regularly. The water draws from fractionator and stripper tower overhead drums in hydroprocessing and catalytic reformer units should also be checked regularly.

3.37.8 Related Mechanisms

Ammonium chloride corrosion (3.6), Cl^- SCC (3.17), and aqueous organic acid corrosion (3.7).

3.37.9 References

1. *ASM Handbook—Corrosion*, Volume 13, ASM International, Materials Park, OH.
2. A. Bagdasarian et al., "Crude Unit Corrosion and Corrosion Control," Paper No. 615, *Corrosion/96*, NACE International, Houston, TX.
3. NACE Publication 34105, *Effect of Nonextractable Chlorides on Refinery Corrosion and Fouling*, NACE International, Houston, TX.

3.38 Hydrofluoric Acid Corrosion

3.38.1 Description of Damage

Corrosion by water containing dilute hydrofluoric (HF) acid can result in high rates of general or localized corrosion and may be accompanied by hydrogen cracking, blistering, and/or HIC/SOHIC. (See 3.41 and 3.67.) In refining, it is associated with HF acid alkylation units.

3.38.2 Affected Materials

- a) Carbon steel, copper-nickel alloys, Alloy 400.
- b) Low-alloy steels, 300 series SS, and 400 series SS are susceptible to corrosion and/or cracking and are generally not suitable for HF service.
- c) Nickel-based alloys such as Alloy C276 have been used in some applications.

3.38.3 Critical Factors

- a) HF acid concentration (water content), temperature, alloy composition, and the presence of contaminants including oxygen and sulfur compounds are the controlling factors.
- b) Corrosion rates increase with increasing temperature and decreasing HF concentration (increasing water content), as shown in Figure 3-38-1 and Figure 3-38-2.
- c) Carbon steel forms a protective fluoride scale in dry (anhydrous), fresh HF, which enables a very low general corrosion rate in anhydrous HF.
- d) HF containing dissolved water (rich HF) is created when the fresh acid has picked up water as it encounters residual moisture in the feed and isobutane entering an HF alkylation unit. This water-bearing acid can still form a tight protective fluoride scale on carbon steel (e.g. in the reactor settler circuit) but can be impacted by:
 - 1. water content, which if operated at > 1.5 wt % in acid can increase the general corrosion rates; and
 - 2. higher temperatures, which can increase the general corrosion rates.
- e) Rich HF (e.g. as sent to regeneration or as carryover into fractionation), when subject to a phase change (vaporization and condensation), can cause significant localized corrosion of carbon steel because the phase-changing rich HF reaches a very corrosive azeotropic concentration. (An azeotrope is a constant boiling temperature mixture of liquids.) The amount and location of corrosion are impacted by:
 - 1. the amount of water in the rich HF, which will determine the amount of corrosive azeotrope that can form;
 - 2. the amount of rich HF carryover, as determined by reactor circuit operating conditions, with greater amounts of rich HF contributing to increased amounts of azeotrope formation; and
 - 3. changes in the temperature and pressure profiles in the fractionation section, which will determine locations where phase changes occur.
- f) Streams with entrained rich HF, such as in the fractionation overhead system where phase changes do not occur, will be subject to general corrosion except for possible residual element (RE) effects.
- g) Dead-legs in fractionation can be subject to localized corrosion and iron fluoride fouling under the following circumstances:
 - 1. In the upper sections of fractionation where entrained rich HF can reach phase change conditions in dead-legs. Operational parameters that contribute to rich HF carryover will increase the potential for dead-leg corrosion.

2. In the hotter, lower sections of fractionation where organic fluorides will thermally decompose into free HF, which can accumulate in extended dead zones (e.g. PSV headers) and combine with residual waters to cause localized corrosion and iron fluoride scaling. Operational parameters within the reactor/settler will determine the amount of fluorides available for contributing to this corrosion and fouling.
- h) Regeneration of rich HF to remove water and acid soluble oils is done at elevated temperatures that require the use of Alloy 400, which can be subject to various corrosion exposures.
 1. Preheating rich HF (feed or entrained in isobutane stripping medium) above 160 °F (70 °C) will trigger azeotropic corrosion and require the use of Alloy 400, which will be subject to a low level of general corrosion.
 2. Within the regeneration/rerun column, the acid is concentrated into the azeotrope, which corrodes Alloy 400 at a higher rate. Higher temperatures will increase the corrosivity of this material.
 3. Hot HF vapor from the regenerator/rerun column prior to cooling can cause corrosion of carbon steel or Alloy 400 if partial condensation occurs and there is still significant water in the vapor.
- i) Downstream of alumina treaters/defluorinators, the stream is water rich with a small amount of HF that if allowed to condense prior to KOH treating will create dilute HF, which will cause localized corrosion condition on carbon steel. This corrosion can be impacted by:
 1. breakthrough of free HF from the defluorinators, and
 2. the cooling temperature profile through to the KOH treater.
- j) The acid relief header (ARH) and acid relief neutralizer (ARN) will be exposed to potential dilution of rich HF, which will then cause higher carbon steel corrosion rates. This corrosion is impacted by:
 1. moisture ingress into the ARH from nonacid streams or wet purge gases,
 2. inadequate liquid knockout facilities or procedures to remove excess acid into the ARN, and/or
 3. inadequate ARN neutralization facilities or procedures. Initial contact zones within the neutralizer often require Alloy 400 construction.
- k) In carbon steel, the RE content of the base metal and weld metal may have an effect on corrosion rates in certain parts of the unit. This RE content refers to trace elements, primarily %C, %Cu, %Ni, and %Cr, that are present in carbon steel as the result of the steel manufacturing process. (References 1 to 4, 10) The impact of RE varies throughout the unit.
 1. Higher-RE welds and components preferentially corrode in streams with a significant quantity of entrained rich HF.
 2. Higher-RE welds in rich HF have been reported to corrode at higher rates, particularly at higher operating water levels or higher operating temperatures.
 3. High-RE components and welds corrode at substantially higher rates in phase change (azeotropic) exposure zones.
 4. Low-RE components and welds corrode at substantially higher rates when galvanically coupled to high-RE components in dilute HF exposure zones.
- l) Industry guidelines regarding RE content have been developed and implemented into some industry consensus standards as indicated below. A more detailed discussion of these guidelines is outlined in References 1 and 2.
 1. When %C \geq 0.18 wt % (some base metals), (%Cu + %Ni) should be < 0.15 wt %.

2. When %C < 0.18 wt % (weld metal, some base metals), (%Cu + %Ni + %Cr) should be < 0.15 wt %.
- m) Severe corrosion can occur when HF leaks into cooling water or steam due to the dilution of HF.
- n) Oxygen contamination increases the corrosion rate of carbon steel and promotes accelerated corrosion and SCC of Alloy 400. (See 3.41.)
- o) Modified HF (with additive) used in some units has unique corrosion factors that are not included in this discussion.

3.38.4 Affected Units or Equipment

- a) Piping and equipment in the HF alkylation unit; flare piping and downstream units exposed to acid carryover are also affected.
- b) Trace HF circuits can experience very high corrosion rates. A minimal amount of residual moisture can quickly yield a 10 % to 50 % HF acid-in-water concentration in a trace circuit, resulting in aggressive corrosion.
- c) Most equipment is made from carbon steel with the exception of following, which are usually made partially or completely from Alloy 400.
1. Heated acid and acid-containing streams to the rerun/regenerator tower.
 2. HF acid rerun/regenerator tower and ASO/CBM drain systems.
 3. ARN acid/neutralizer contact zones.
- d) High corrosion rates have been observed in:
1. piping and equipment operating above 150 °F (65 °C);
 2. dead-legs including inlets to relief valves, as well as small-bore vents and drains; and
 3. rich HF phase change locations including:
 - preheated feed exchangers and piping to the inlet of the isostripper, depropanizer, and HF stripper towers;
 - isostripper, depropanizer, and HF stripper tower tops; and
 - piping and exchangers off the top of the isostripper, depropanizer, and HF stripper or propane stripper where overhead vapors condense;
 4. dead-legs, piping and exchangers between the alumina treaters/defluorinator and the KOH treater due to dilute HF exposure;
 5. the ARH;
 6. flange faces, particularly in rich HF phase change locations;
 7. DMWs between Alloy 400 and CS in any acid service;
 8. heat exchanger bundles that condense rich-HF-containing streams such as the isostripper overhead and recycle isobutane as well as the depropanizer overhead coolers; and

9. heat exchanger bundles that heat rich-HF-containing streams such as the acid vaporizer, isostripper, and depropanizer preheat exchangers.
- e) Severe fouling due to iron fluoride corrosion product has been observed in:
1. the tops of the isostripper, depropanizer, and HF stripper towers as well as the piping and heat exchangers off of them; and
 2. dead-legs (e.g. PSV headers) in the bottoms of the isostripper, depropanizer, and HF stripper towers.

3.38.5 Appearance or Morphology of Damage

- a) Corrosion is in the form of:
1. general corrosion in fresh HF and rich HF,
 2. localized corrosion of welds in rich HF,
 3. localized corrosion in phase change rich HF,
 4. localized corrosion in entrained rich HF,
 5. general and localized corrosion of Alloy 400 in hot rerun/regenerator service,
 6. localized corrosion in dead-legs in entrained rich HF or fluoride defluorination services,
 7. localized corrosion in dilute HF, and
 8. localized corrosion in the ARH and ARN.
- b) Preferential corrosion may not always conform to behavior predicted by the RE guidelines in API 751. ([Figure 3-38-3](#) to [Figure 3-38-6](#))
- c) DMWs between Alloy 400 and carbon steel will lead to preferential galvanic corrosion of the carbon steel (and potentially DMW cracking) if exposed to acid.
- d) Corrosion may be accompanied by cracking due to hydrogen stress cracking, blistering, and/or HIC/SOHIC damage. ([Figure 3-38-8](#))
- e) Significant fouling due to iron fluoride scales may also accompany corrosion.
- f) Alloy 400 shows uniform loss in thickness but is not accompanied by significant scaling.
- g) Alloy 400 is susceptible to SCC when in contact with moist HF vapors in the presence of oxygen. (See [3.41.](#))

3.38.6 Prevention/Mitigation

- a) Carbon steel operating above 150 °F (65 °C) should be closely monitored for loss in thickness and may need to be upgraded to Alloy 400.
- b) Corrosion can be mitigated by careful unit operational controls such as:
1. maintaining strict controls on the water content of the circulating rich acid,
 2. controlling the rate and temperature of the reactor/settler system,
 3. minimizing acid carryover from the settler into fractionation,

4. controlling feed quality and the reactor to control fluoride formation,
 5. controlling the temperature in fractionation to avoid phase changes outside of the exchangers,
 6. controlling the temperature in the rerun/regenerator,
 7. controlling HF stripper operation to avoid free HF into bottoms and defluorinators,
 8. controlling the defluorinator to avoid free HF breakthrough and dilute HF condensation, and
 9. controlling ARH and ARN neutralization to ensure full neutralization of relief streams.
- c) PWHT of carbon steel can reduce the problems associated with SOHIC as well as minimizing accelerated preferential corrosion in the HAZ of welds.
- d) Alloy 400 (solid or clad) can be used to eliminate the problems associated with blistering and HIC/SOHIC.

3.38.7 Inspection and Monitoring

- a) UT can be used to monitor for corrosion loss. Because the carbon steel corrosion rate in HF acid can be highly localized, with rates having been found to vary as much as 30 % in a single component, AUT, hand scanning, or use of multiple single point readings per component may be needed for effective assessment.
- b) Profile RT can be used to monitor for thickness loss in drains, vents, low points, swages, and small-bore piping, as well as fittings, where low-RE and high-RE materials are coupled.
- c) PAUT can be used to perform in situ crevice corrosion monitoring on flange faces. The iron fluoride scale conforms to the shape of the flange face, which makes VT difficult when the flanges are separated.
- d) GWT testing, while typically not providing the accuracy needed as compared to standard UT, can be a useful screening tool to identify locations for follow-up with UT.
- e) Permanently mounted thickness monitoring sensors can be used.
- f) Special emphasis programs to monitor RE corrosion, small-bore piping, mix point, dead-leg, and flange face corrosion (as well as blistering and HIC/SOHIC) are outlined in API 751.
- g) RE content of carbon steel components should be monitored in accordance with API 751 guidelines. Potential localized corrosion of piping components and/or welds should be inspected for in accordance with API 751.

3.38.8 Related Mechanisms

Hydrogen stress cracking in HF acid (3.41), hydrogen blistering and HIC/SOHIC (covered in *Wet H₂S Damage* 3.67), HF acid SCC of nickel alloys (3.39), and DMW cracking (3.26).

3.38.9 References

1. API Recommended Practice 751, *Safe Operation of Hydrofluoric Acid Alkylation Units*, American Petroleum Institute, Washington, DC.
2. NACE Publication 5A171, *Materials for Storing and Handling Commercial Grades of Aqueous Hydrofluoric Acid and Anhydrous Hydrogen Fluoride*, NACE International, Houston, TX.
3. H.H. Hashim and W.L. Valerioti, "Corrosion Resistance of Carbon Steel in HF Alkylation Service," *Materials Performance*, November 1993, p. 50.

4. A. Gysbers et al., "Specification for Carbon Steel Materials for Hydrofluoric Acid Units," Paper No. 03651, *Corrosion/2003*, NACE International, Houston, TX.
5. J.D. Dobis, D.R. Clarida and J.P. Richert, "Survey Reveals Nature of Corrosion in HF Alkylation Units," *Oil and Gas Journal*, Vol. 93, No. 10, March 6, 1995, pp. 63–68.
6. H.S. Jennings, "Materials for Hydrofluoric Acid Service in the New Millenium," Paper No. 01345, *Corrosion/2001*, NACE International, Houston, TX.
7. J.D. Dobis, D.G. Williams and D.L. Bryan Jr., "The Effect of Operating Conditions on Corrosion in HF Alkylation Units," *Corrosion/04*, Paper No. 645, NACE International, Houston, TX, 2004.
8. J.D. Dobis, "The Top Ten Corrosion Issues Affecting HF Alkylation Units," Paper No. 07570, *Corrosion/2007*, NACE International, Houston, TX.
9. H.P.E. Helle, *Guidelines for Corrosion Control in HF-alkylation Units*, Second Edition, New Plantation, Delft, Netherlands, April 1993.
10. C.J. Schulz, "Corrosion Rates of Carbon Steel in HF Alkylation Service," Paper No. 06588, *Corrosion/2006*, NACE International, Houston, TX.
11. A.C. Gysbers, J. Wodarczyk, F. Sapienza, and T. Copeland, "Localized Corrosion of Carbon Steel from Hydrofluoric Acid—An Update," *Materials Performance*, Vol. 56, No. 2, NACE International, Houston, TX, February 2017.

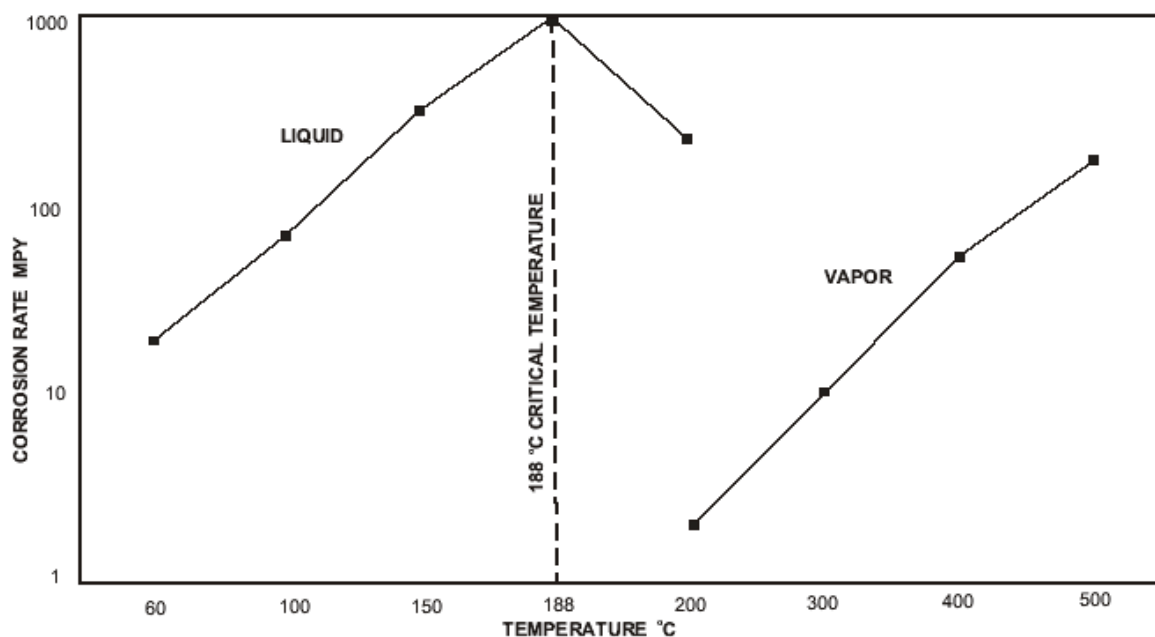


Figure 3-38-1—Corrosion rate as a function of temperature for carbon steel in anhydrous HF acid under stagnant conditions in 100-hr laboratory test. (Reference 2)

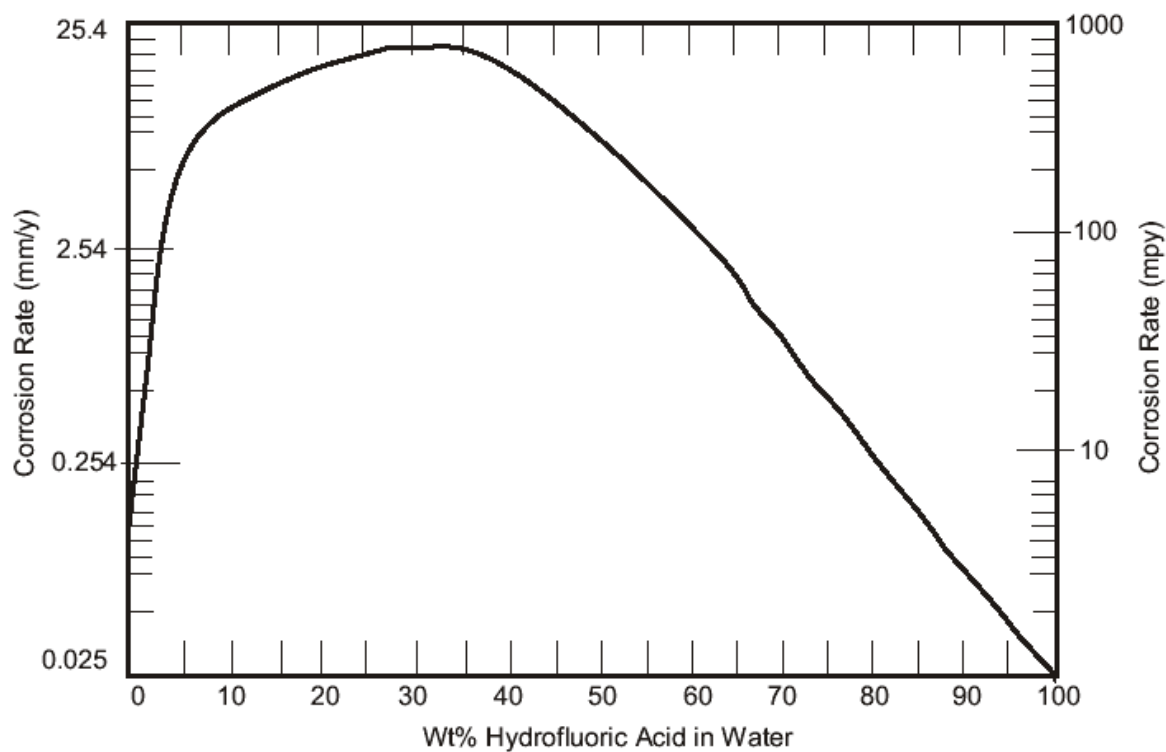


Figure 3-38-2—The corrosion rate of carbon steel at 70 °F to 100 °F (20 °C to 40 °C) based on laboratory testing and field experience at low-flow and no-flow conditions. (Reference 2)



Figure 3-38-3—Cross section of a carbon steel pipe showing preferential corrosion of the pipe with high RE content on the right, as compared to the low-RE pipe section to the left of the weld. (Reference 3)



**Figure 3-38-4—Ruptured NPS 3 Sch. 80 [0.216 in. (5.5 mm) wall thickness] depropanizer feed line operating < 120 °F (50 °C). RE content is as follows.
Both base metals: %C > 0.18 wt %; %Cu + %Ni < 0.15.
Weld metal: %Cu + %Ni + %Cr < 0.15.**

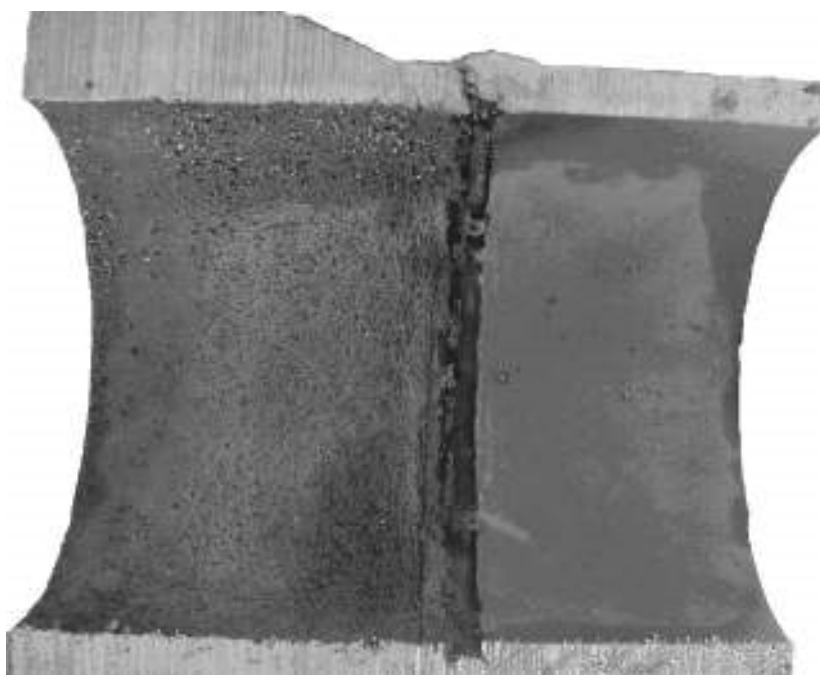


Figure 3-38-5—A cross section of a line in fresh acid service showing accelerated corrosion of the weld and base metal of the component on the left. (Reference 8)



Figure 3-38-6—Accelerated corrosion in the HAZ of a carbon steel weldment. RE content is as follows. (Reference 8)
Both base metals: %C > 0.18 wt %; %Cu + %Ni < 0.15.
Weld metal: %Cu + %Ni + %Cr < 0.15.



Figure 3-38-7—HF corrosion at a manway in HF acid storage service.



Figure 3-38-8—Internal blister caused by HF corrosion near the top of a 1.2-in.-thick carbon steel tower in an HF alkylation unit. The maximum measured dimensions of the blister were 2 ft high and 20 ft long (circumferentially). The hanging weight of an adjacent tray, which was also badly corroding, may have contributed to the location and size of the blister.

3.39 Hydrofluoric Acid Stress Corrosion Cracking of Nickel Alloys

3.39.1 Description of Damage

Surface-initiated environmental cracking of nickel alloys under the combined action of tensile stress and vapor-containing hydrofluoric acid environments, either anhydrous or wet. SCC is triggered by the presence of cupric fluoride (CuF_2), which is created by the exposure of normally protective CuF to an oxidizing agent that most commonly is oxygen in air, resulting from air ingress while onstream or during turnarounds, or as a contaminant in purge gases.

3.39.2 Affected Materials

- a) Alloy 400 has a nickel content in the susceptible regime.
- b) Alloy K-500 in its high-strength, strain-hardened condition is very susceptible.
- c) The Ni-Cr-Mo alloys including Alloy C-22, Alloy 59, Alloy C-2000, Alloy 625, Alloy 686, and Alloy C-276, in both wrought and cast form, are sometimes susceptible to SCC in HF service when CuF_2 is present. They also are sometimes susceptible to intergranular corrosion and environmental cracking if stressed or cold worked.

3.39.3 Critical Factors

- a) Oxidizing agent exposure in the presence of CuF and HF.
 - 1. Typically, oxygen exposure is due to air ingress with residual HF present.
 - 2. High levels of oxygen can also exist in in purge gases (nitrogen, fuel gas) used in acid storage, acid relief, PSV headers, etc.
- b) High levels of residual stress such as in cold-worked tubing, u-bends, and as-welded welds.
- c) High hardness levels, particularly in aged Alloy K-500.

3.39.4 Affected Units or Equipment

- a) HF alkylation units employing nickel alloys for equipment pressure boundaries, internals, instruments, valve components (especially stems), and pump components. ([Figure 3-39-1](#) and [Figure 3-39-2](#))

3.39.5 Appearance or Morphology of Damage

- a) Presence of CuF_2 is indicated by a green crystalline deposit. ([Figure 3-39-1](#))
- b) Annealed material will suffer intergranular corrosion and eventual cracking.
- c) Cold-worked material will suffer transgranular cracking.

3.39.6 Prevention/Mitigation

- a) Stress relief heat treatment will prevent SCC in cold-worked (formed components including u-bends) or welded Alloy 400.
 - 1. A minimum heat treatment temperature of 1300 °F (705 °C) should be used.
- b) The hardness of Alloy K-500 components should be limited to a maximum of HRC 30.
- c) Avoid use of Alloy 400 or Alloy K-500 for pressure boundary bolting.

- d) Nickel alloy bolting for internals should be in the fully annealed form, and torque controls should be employed to avoid overtorqueing.
- e) Purge/vent practices that avoid creating a vacuum and allowing air ingress should be employed.
- f) Free HF should be completely removed and neutralized before opening equipment to air.
- g) A maximum oxygen content of <100 ppm should be specified for purge gases.

3.39.7 Inspection and Monitoring

- a) PT can be used for identifying cracks on suspected exposed components e.g. those with green crystals on the surface.
- b) Purge gases should have ongoing monitoring of oxygen levels.

3.39.8 Related Mechanisms

- a) CuNi Alloys (UNS C70600 and C71500) can suffer denickelification pitting corrosion when exposed to moist HF and air. (See *Dealloying*, 3.24.) Highly cold worked components, e.g. u-bends with a tight bend radius, can suffer SCC. Cold-worked u-bends should be heat treated to a minimum of 950 °F (510 °C).
- b) LME (3.42) can occur in Alloy 400 due to Hg contamination.

3.39.9 References

1. NACE Publication 5A171, *Materials for Storing and Handling Commercial Grades of Aqueous Hydrofluoric Acid and Anhydrous Hydrogen Fluoride*, NACE International, Houston, TX.
2. MTI Publication MS-4, *Hydrogen Fluoride and Hydrofluoric Acid*, Materials Technology Institute of the Chemical Process Industries, St. Louis, MO.
3. *Materials of Construction Guideline for Anhydrous Hydrogen Fluoride*, Hydrogen Fluoride Industry Practices Institute (HFIP), Washington, DC.
4. API Recommended Practice 751, *Safe Operation of Hydrofluoric Acid Alkylation Units*, American Petroleum Institute, Washington, DC.
5. H.R. Copson and C.F. Cheng, "Stress Corrosion Cracking of Monel in Hydrofluoric Acid," *CORROSION*, Vol.12(12), 1956, pp. 71–77.
6. L. Graf and W. Wittich, Untersuchung von Sonderfällen der Spannungskorrosion bei homogenen, nicht übersättigten Mischkristallen und der hierbei auftretenden elektrochemischen Prozesse, *Werkstoffe und Korrosion/Materials and Corrosion*, Vol. 17, 1966, pp. 385–405.
7. J. D. Dobis, "The Top Ten Corrosion Issues Affecting HF Alkylation Units," Paper No. 07570, *Corrosion/2007*, NACE International, Houston, TX.



Figure 3-39-1—HF SCC of an Alloy 400 vent line in an acid dump system. (Reference 7)



Figure 3-39-2—HF SCC of Alloy 400 instrument tubing. (Reference 7)

3.40 Hydrogen Embrittlement

3.40.1 Description of Damage

Hydrogen embrittlement (HE) is the loss in strength, ductility, and/or fracture toughness of susceptible materials due to the penetration and diffusion of atomic hydrogen. HE can lead to brittle cracking. It can occur during manufacturing, welding, or from services that charge hydrogen into the metal.

3.40.2 Affected Materials

Low-alloy steels, high-strength steels, 400 series SS, precipitation hardenable stainless steel, duplex stainless steel, and some high-strength nickel-based alloys. Carbon steel can suffer HE if hardened by cold work or welding. Typically, a steel has to have hardness greater than Rockwell hardness number (HRC) 22 to be susceptible to HE cracking in the most severe environments. Higher strength/hardness can be tolerated in milder environments. (For the purposes of this section, blistering and HIC are not considered examples of HE. See [3.67](#), *Wet H₂S Damage*.)

3.40.3 Critical Factors

a) The following five conditions must be satisfied.

1. The material must be susceptible.
2. Hydrogen must be present at a critical concentration within the material.
3. The strength/hardness level must be high enough and the microstructure must be susceptible to HE.
4. A stress above the threshold for HE must be present from residual stresses and/or applied stresses.
5. The temperature must be in the embrittling and cracking range. HE generally diminishes with increasing or decreasing temperature away from ambient.

b) The hydrogen can come from the following.

1. Welding—If wet electrodes or electrodes with a high moisture content flux are used, hydrogen can be charged into the material. Cracking in a susceptible material from this cause is often called delayed cracking or underbead cracking.
2. Corrosion Reactions—Most aqueous corrosion reactions produce hydrogen. Wet H₂S services and HF acid services in which atomic hydrogen diffuses into the metal as the result of the corrosion reaction are two of the most severe and common examples. (See *Wet H₂S Damage*, [3.67](#), and *Hydrogen Stress Cracking in Hydrofluoric Acid*, [3.41](#).) Sulfur and arsenic act as atomic hydrogen recombination poisons in wet H₂S and HF acid environments, respectively, that inhibit the reaction of atomic hydrogen to form H₂ gas, thus enabling a higher percentage of hydrogen atoms to diffuse into the metal. Cyanide can also promote hydrogen charging by forming a complex with the surface films rendering them less protective. This in turn results in increased corrosion with associated increases in atomic hydrogen production. In very high strength, highly susceptible steels, the corrosion reaction alone, without the need for a recombination poison, can lead to HE cracking.
3. Service in high-temperature [$>400^{\circ}\text{F}$ (205°C)] hydrogen gas atmospheres. Molecular hydrogen dissociates to form atomic hydrogen that can diffuse into the metal.
4. Cleaning and pickling in acid solutions.
5. Manufacturing—Melting practices or manufacturing processes, particularly where susceptible components are plated, e.g. high-strength bolts plated with cadmium, can lead to HE cracking. This is sometimes called hydrogen flaking.

6. Cathodic Protection—Hydrogen is formed on the surface of the protected metal, which can lead to HE cracking if the metal is susceptible.
- c) The effect is generally most pronounced at ambient temperatures, decreases rapidly above 150 °F (65 °C), and effectively disappears above about 300 °F (150 °C). The temperature above which it is no longer a practical concern in a given circumstance varies depending on the susceptibility of the material and the hydrogen charging environment.
 - d) HE affects static properties to a much greater extent than impact properties. If the hydrogen is present and a sufficient stress is applied, failure can occur quickly.
 - e) The amount of trapped hydrogen depends on the environment, surface reactions, and the presence of hydrogen traps in the metal such as imperfections, inclusions, and pre-existing flaws or cracks.
 - f) The amount of hydrogen needed to have a measurable effect on the mechanical properties varies with the strength level, microstructure, and heat treatment for the alloy. In some cases, thresholds of critical hydrogen concentrations have been established.
 - g) Stress to cause cracking can result from cooling during manufacture or from PWHT temperatures, residual stresses from welding, or applied loads.
 - h) Thick wall components can be more vulnerable due to increased thermal stress during cool-down from operating temperatures, high restraint and potentially high stress concentrations at flaws or cracks, and because they take longer for hydrogen to diffuse out.
 - i) In general, as strength increases, susceptibility to HE increases. Certain microstructures, such as untempered martensite, are more susceptible at the same strength level than tempered martensite. Carbon steel that is severely hydrogen charged will have lower fracture toughness than with no hydrogen.
 - j) HE is reversible as long as cracking has not occurred. The hydrogen can be baked out at elevated temperature [400 °F (205 °C) or higher, typically around 600 °F (315 °C)].

3.40.4 Affected Units or Equipment

- a) Cr-Mo reactors, drums, exchanger shells, and piping in hydroprocessing units and catalytic reforming units can be susceptible to cracking if the weld HAZ hardness exceeds Brinell hardness number (HB) 225.
- b) Storage spheres are often made of higher-strength steels (>70 ksi specified minimum tensile strength) than common pressure vessel steels and are therefore more susceptible than most other refinery equipment if not stress relieved.
- c) Bolts and springs made of high-strength steel are very prone to HE cracking. Components that have a tensile strength above 150 ksi can absorb hydrogen during electroplating and crack prior to being put in service.
- d) Other services where HE is a concern include where susceptible materials such as high-strength valve components, instrument components, and similar are exposed to wet H₂S in FCC, hydroprocessing, amine, SW, and other H₂S-containing services, as well as HF in alkylation units. For these services, equipment manufactured using HE-resistant materials for the potentially susceptible components is typically selected, with the materials meeting the requirements of, e.g. NACE MR0103/ISO 17945. (See *Wet H₂S Damage*, [3.67](#), and *Hydrogen Stress Cracking in Hydrofluoric Acid*, [3.41](#).)
- e) Carbon steels normally used for vessels, piping, and other equipment in most refining applications have low strength/hardness and are usually not susceptible to HE as long as typical welding procedures and precautions regarding controlling the moisture in welding consumables are followed.

3.40.5 Appearance or Morphology of Damage

- a) HE by itself is not visible. It only appears when cracking occurs.
- b) Cracking resulting from HE can initiate subsurface but in most cases is surface breaking. (Figure 3-40-1 and Figure 3-40-2)
- c) HE cracking occurs at locations of high residual or tri-axial stresses (notches, restraint) and where the hardness and microstructure are conducive, such as in weld HAZs.
- d) On a macro-scale, there is typically little evidence of deformation. Cracking will appear to be brittle, with visible fracture surfaces having a brittle appearance. On a microscale, the material will contain less ductile fracture surface but must often be compared to a fracture without the presence of hydrogen.
- e) Under metallographic examination, cracking is typically branched. In higher-strength steels, cracking is often intergranular. (Figure 3-40-1)

3.40.6 Prevention/Mitigation

- a) Depending on the source of the hydrogen, choose an alloy composition, fabrication/heat treatment method, and hardness limit suitable for the intended service.
- b) Control the hardness of hardenable steels and PWHT to reduce hardness and temper residual stresses.
- c) During welding, use dry, low-hydrogen electrodes and preheating methods.
- d) If hydrogen diffused into the metal during welding is a concern, an elevated temperature bake-out [400 °F (205 °C) or higher, typically around 600 °F (315 °C)] may be required to drive the hydrogen out prior to cooling to ambient temperature.
- e) If hydrogen is expected to have diffused into the metal during operation, a similar elevated temperature bake-out [400 °F (205 °C) or higher, typically around 600 °F (315 °C)] may be required to drive out the hydrogen out prior to welding for maintenance or repair.
- f) Heavy wall equipment in hot hydrogen service typically requires controlled shutdown and start-up procedures to control the pressurization sequence as a function of temperature.
- g) In corrosive aqueous services, a protective lining, cladding, or weld overlay can be applied to prevent the surface hydrogen reactions.
- h) Avoid the use of cadmium or other plating on high-strength bolts.

3.40.7 Inspection and Monitoring

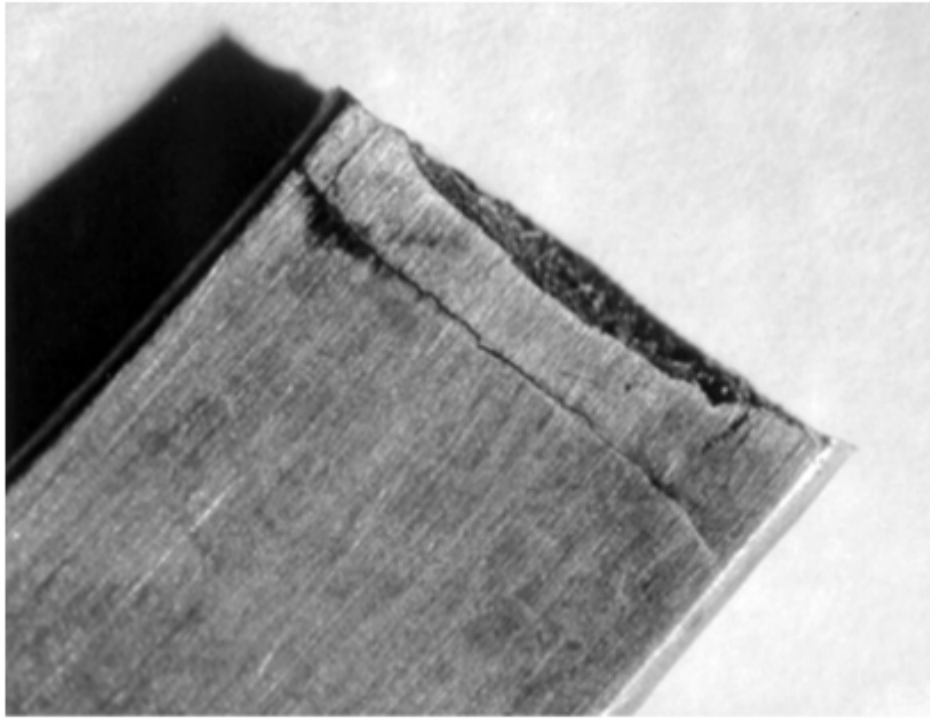
- a) PT, MT, or WFMT can be used for surface cracking inspection.
- b) Angle beam (e.g. SWUT or PAUT) may also be useful in finding as well as sizing HE cracks.
- c) RT often is not sufficiently sensitive to detect HE cracks.
- d) VT is not reliable for finding HE cracks.
- e) If the source of hydrogen is a low-temperature aqueous environment, hydrogen flux can be monitored using specialized instruments.

3.40.8 Related Mechanisms

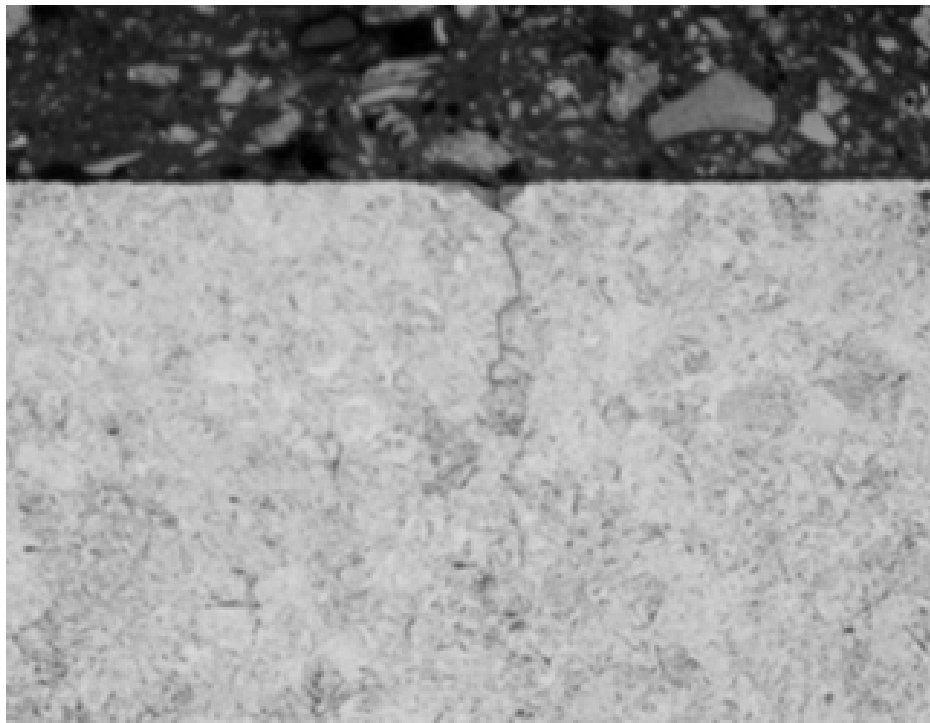
Also known as underbead cracking, delayed cracking, hydrogen-assisted cracking, and hydrogen flaking, SSC (covered in 3.67) and hydrogen stress cracking in HF acid (3.41) are closely related forms of HE.

3.40.9 References

1. W.E. Erwin and J.G. Kerr, *The Use of Quenched and Tempered 2¼Cr-1Mo Steel for Thick Wall Reactor Vessels in Petroleum Refinery Processes: An Interpretive Review of 25 Years of Research and Application*, WRC Bulletin 275, Welding Research Council, Shaker Heights, OH.
2. R.S. Treseder, "Guarding Against Hydrogen Embrittlement," *Chemical Engineering Magazine*, Chemical Week Publishing, June 1981.
3. *ASM Handbook—Corrosion*, Volume 13, ASM International, Materials Park, OH.
4. *Corrosion Basics—An Introduction*, NACE International, Houston, TX, 1984, pp. 120–121.
5. NACE MR0103/ISO 17945, *Petroleum, petrochemical and natural gas industries—Metallic materials resistant to sulfide stress cracking in corrosive petroleum refining environments*, NACE International, Houston, TX.



(a)

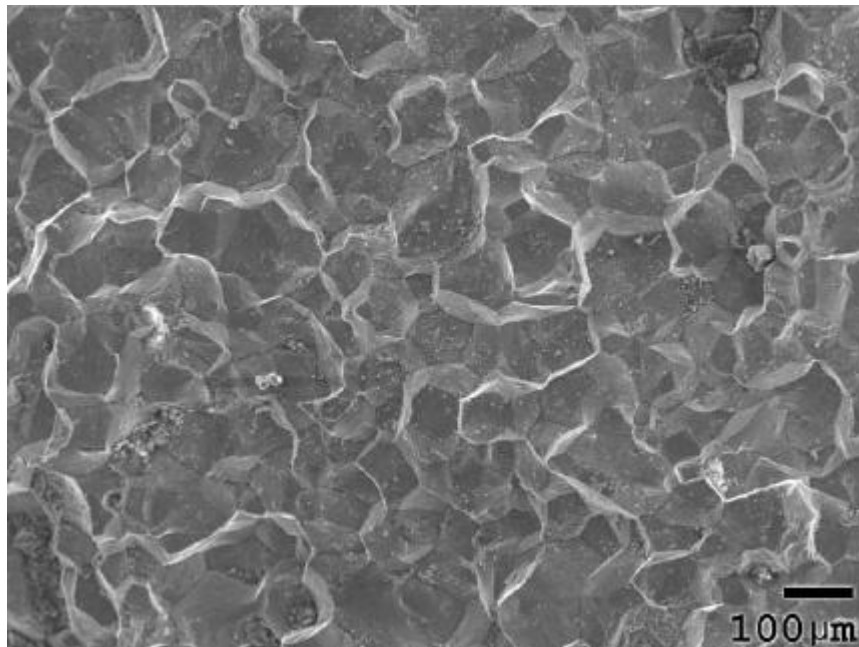


(b)

**Figure 3-40-1—(a) Cracking due to HE of a high-strength steel tube.
(b) Intergranular crack emanating from surface in the tube.**



(a)



(b)

Figure 3-40-2—(a) HE of a martensitic stainless steel pump component. (b) High-magnification fractograph of the fracture surface showing intergranular nature of the cracking.

3.41 Hydrogen Stress Cracking in Hydrofluoric Acid

3.41.1 Description of Damage

Hydrogen stress cracking is a form of environmental cracking that can occur in high-strength low-alloy (HSLA) steels and carbon steels with highly localized zones of high hardness in the weld metal and HAZ, as the result of exposure to aqueous HF acid environments.

3.41.2 Affected Materials

Carbon steel and low-alloy steels.

3.41.3 Critical Factors

- a) Steel hardness, strength, and stress are the critical materials factors.
- b) Susceptibility increases with increasing hardness. Steels with hardness levels above HRC 22 (HB 237) are highly susceptible. Time-to-failure decreases as the hardness, which directly correlates to strength level, increases, i.e. higher-strength steels are more susceptible.
- c) Under high levels of applied or residual tensile stress (from cold-forming or welding), embrittlement resulting from the hydrogen charged into the steel by the corrosion reaction in HF [i.e. hydrogen embrittlement (see [3.40](#))] results in cracking of susceptible steels.
- d) Cracking may occur very rapidly, within hours after exposure to the HF environment, or considerable time may pass before cracking initiates.
- e) In low-alloy steels, but also potentially in carbon steel, particularly with low-heat-input welds, hard microstructures may arise in the weld and HAZs as the result of high hardenability and inadequate heat treatment.

3.41.4 Affected Units or Equipment

- a) All piping and equipment exposed to HF acid at any concentration with hardness levels above the recommended limit are subject to hydrogen stress cracking.
- b) HSLA steels used for components such as ASTM A193-B7 bolts as well as valve and compressor parts are susceptible.
- c) ASTM A193-B7M bolts can be susceptible if overtorqued.

3.41.5 Appearance or Morphology of Damage

- a) This mode of cracking can only be confirmed by metallographic examination. The cracking will be primarily transgranular in carbon steel. In high-strength steel, it may be intergranular.
- b) Cracks are surface breaking and are usually associated with weldments.

3.41.6 Prevention/Mitigation

- a) Weld procedure qualification, chemistry controls, and PWHT are the methods used to avoid high-hardness HAZs.

b) Welding controls are employed to minimize the potential for hard welds and HAZs in carbon steel and low-alloy steels. (See e.g. NACE SP0472.) Typical options used in HF service include the following.

1. Use of carbon steels with carbon equivalent (CE) and RE chemistry controls. CE is defined as:

$$CE = \%C + \%Mn/6 + \%(\text{Cr} + \text{Mo} + \text{V})/5 + \%(\text{Cu} + \text{Ni})/15.$$

2. RE controls are described in *Hydrofluoric Acid Corrosion*, 3.38.3 k).

3. PWHT, which is beneficial in reducing the hardness and residual stresses that contribute to hydrogen stress cracking.

4. Use of exempt welding process/filler metal combinations.

5. Production weld metal hardness testing to ensure hardness < HB 200.

c) ASTM A193 grade B7M bolts are softer and lower strength than B7 bolts and are considered resistant to cracking.

d) Alloy cladding or nonmetallic coatings that provide an effective barrier and protect the surface of the steel from corrosion and hydrogen permeation will prevent cracking.

e) Alloy 400 is not susceptible to this form of cracking but may be susceptible to SCC, particularly in the non-stress-relieved condition. (See 3.39.) DMW between Alloy 400 and carbon steel may also be susceptible to cracking when exposed to HF. (See 3.27.)

3.41.7 Inspection and Monitoring

a) Surface-breaking cracks can be found by PT, MT, or WFMT.

b) Angle beam UT (SWUT or PAUT) may also be useful for finding or determining the depth of cracks. Straight beam UT can identify cracked bolts.

c) ACFM can be used in lieu of WFMT for crack detection; however, it is highly operator dependent.

d) Hardness testing of weld metal and bolting is the best method to determine the susceptibility of suspect material.

1. Zones of high hardness can sometimes be found on the process side in weld cover passes and attachment welds that are not tempered (softened) by subsequent passes.

3.41.8 Related Mechanisms

This is the same mechanism (i.e. HE, 3.40) that is responsible for SSC in wet H₂S environments except that HF acid corrosion is generating the hydrogen. Blistering, HIC, and SOHIC damage in HF acid is similar to that found in wet H₂S. (See 3.67.) See also *Hydrofluoric Acid Stress Corrosion Cracking of Nickel Alloys*, 3.39.

3.41.9 References

1. J.D. Dobis, D.R. Clarida and J.P. Richert, "Survey Reveals Nature of Corrosion in HF Alkylation Units," *Oil and Gas Journal*, Vol. 93, No. 10, March 6, 1995, pp. 63–68.
2. J. Gutzeit, R.D. Merrick, and L.R. Scharfstein, "Corrosion in Petroleum Refining and Petrochemical Operations," *Metals Handbook*, Volume 13, ASM International, Materials Park, OH, 1987, pp. 1262–1287.
3. NACE SP0472, *Methods and Controls to Prevent In-service Environmental Cracking of Carbon Steel Weldments in Corrosive Petroleum Refining Environments*, NACE International, Houston, TX.

3.42 Liquid Metal Embrittlement

3.42.1 Description of Damage

Liquid metal embrittlement (LME) is a form of cracking that results when certain molten or liquid metals (the embrittler) come in contact with specific alloys. Cracking can be very sudden and brittle in nature. Laboratory experiments have demonstrated that, for some metal/embrittler couples, embrittlement can also occur at temperatures below the embrittler melting point (solid metal embrittlement).

3.42.2 Affected Materials

Many commonly used materials including carbon steel, low-alloy steels, high-strength steels, 300 series SS, nickel alloys, copper alloys, aluminum alloys, and titanium alloys.

3.42.3 Critical Factors

- a) LME occurs in very specific combinations of metals in contact with low-melting-point metals such as zinc, mercury, cadmium, lead, copper, and tin. Combinations of industrial significance are shown in [Table 3-42-1](#).
- b) High tensile stress promotes cracking; however, cracking can initiate simply through contacting the molten metal with the susceptible alloy. Very small quantities of the low-melting-point metal are sufficient to cause LME.
- c) The embrittler can be external to the metal, such as zinc on the surface of stainless steel, or the embrittler can be internal to the metal, such as the lead in a leaded free-machining steel.
- d) Tensile stress contributes to high crack propagation rates. Cracking under load can be extremely rapid such that cracks may pass through the wall within seconds of contact with the molten metal.
- e) In cases where embrittlement is severe, fracture occurs at virtually zero percent strain.
- f) A susceptible metal in contact with or contaminated with a low-melting metal will not crack while at low temperatures but may crack later when the temperature rises above the melting temperature of the low-melting alloy.

3.42.4 Affected Units or Equipment

- a) In refining, LME is relevant and of most concern after a fire, after failure of an instrument containing mercury (Hg) that leaks into or onto equipment, or where the incoming crude contains mercury.
- b) During a fire, molten metals may drip onto or contact a susceptible metal. Examples include melted zinc galvanizing, cadmium electrical housings, cadmium plated bolts, studs, or nuts, tin or lead from solders, and melted copper components.
 - 1. Probably the most relevant example in refining is 300 series SS piping or vessels near or in contact with (or previously rubbed against) galvanized steel where the zinc melts during a subsequent fire and cracks the stainless steel. ([Figure 3-42-1](#) and [Figure 3-42-2](#))
- c) Failure of process instruments that utilize mercury can introduce the liquid metal into refinery streams. ([Figure 3-42-3](#))
- d) Mercury is found in some crude oils and can condense in the atmospheric tower overhead system, thereby embrittling brass, Alloy 400, titanium, or aluminum exchanger components.
- e) LME of aluminum components has occurred in LNG facilities and cryogenic gas plant components due to condensation of liquid mercury.

3.42.5 Appearance or Morphology of Damage

- a) Damage resulting from LME will appear as brittle cracks in an otherwise ductile material. LME can only be confirmed through metallography by the presence of intergranular cracks, usually filled with the low-melting metal.
- b) Techniques such as spectrographic analysis may be required to confirm the presence of the molten metal species.

3.42.6 Prevention/Mitigation

- a) LME can only be prevented by protecting metal surfaces from coming into contact with the low-melting metal. For example, galvanized steel components should not be welded to 300 series SS. 300 series SS should be protected to avoid contact with galvanized components and overspray from inorganic zinc and other zinc-containing coatings.
- b) Once cracking from LME has initiated, grinding out the affected area is unlikely to be an acceptable or practical fix.

3.42.7 Inspection and Monitoring

- a) Cracks are often visually apparent.
- b) Cracks in carbon and low-alloy steels and other ferritic materials can be detected with MT or WFMT examination. For 300 series SS, nickel-based alloys, and other nonmagnetic materials, PT examination can be used.
- c) Inspection for LME after a fire should be focused where molten metal has dripped on equipment and solidified.
- d) Because of the high density of mercury, RT has been used to locate deposits inside equipment, piping, and tubes. A boroscope can also be used to visually detect liquid mercury inside equipment.

3.42.8 Related Mechanisms

LME is also referred to as liquid metal cracking. Nickel alloys are susceptible to a similar mechanism caused by the nickel-nickel sulfide eutectic that forms at 1157 °F (625 °C).

3.42.9 References

1. *ASM Handbook—Failure Analysis and Prevention*, Volume 11, ASM International, Materials Park, OH.
2. C.P. Dillon, *Corrosion Control in the Chemical Process Industries*, Materials Technology Institute (printed by NACE), MTI Publication No 45, Second Edition, St. Louis, MO, 1994, pp. 84–85.

Table 3-42-1—Some LME Couples Susceptible to Embrittlement (See Note)

Susceptible Alloy	Molten Metal
Carbon steel	Lead, cadmium
Low-alloy steel and high-strength steels	Lead, cadmium
300 series SS	Zinc, copper, high-copper brazing alloys
Copper alloys	Mercury, lead, lead-tin solders
Alloy 400	Mercury
Nickel alloys	Mercury, lead
Aluminum alloys	Mercury, tin
Titanium	Mercury

NOTE Laboratory testing has shown that there are other molten metals that will embrittle the susceptible alloys listed. However, the information in Table 3-34-1 is limited to those molten metals known to be of significance to the refining and petrochemical industries.

SKETCH OF PIPE DETAIL RECEIVED FOR ANALYSIS.
VIEW FROM ABOVE.

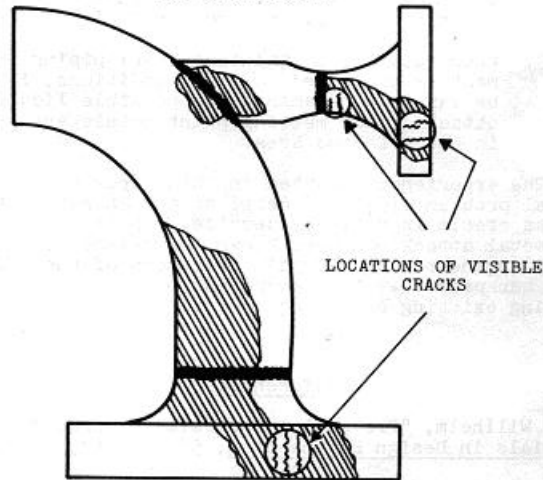


Figure 3-42-1—Sketch of a stainless steel elbow that suffered liquid metal embrittlement as the result of dripping molten zinc during a fire.



Figure 3-42-2—Photomicrograph of a section of the elbow in Figure 3-40-1, illustrating the intergranular nature of zinc-filled cracks in stainless steel.



Figure 3-42-3—LME of Monel caused by mercury in an FCC gas plant overhead drum.

3.43 Mechanical Fatigue (Including Vibration-induced Fatigue)

3.43.1 Description of Damage

- a) Fatigue cracking is a mechanical form of degradation that occurs when a component is exposed to cyclical stresses for an extended period, e.g. from dynamic loading due to vibration, water hammer, or unstable fluid flow, often resulting in sudden, unexpected thru-wall cracking.
- b) These stresses can arise from either mechanical loading or thermal cycling and are typically well below the yield strength of the material. This section focuses on mechanical loading, while the effects of thermal cycling are covered in 3.64 on thermal fatigue.

3.43.2 Affected Materials

All engineering alloys are subject to fatigue cracking although the stress levels and number of cycles necessary to cause failure can vary by material.

3.43.3 Critical Factors

- a) Geometry, stress level, number of cycles, and material properties (strength, hardness, microstructure) are predominant factors in determining the fatigue resistance of a component. The amplitude and frequency of vibrations (related to stress level and number of cycles) in vibrating equipment such as piping are also critical factors. There is a high likelihood of cracking when the input vibrational load is synchronous or nearly synchronizes with the natural or harmonic frequency of the component.
- b) Design Factors—Fatigue cracks usually initiate on the surface at notches or stress risers under cyclic loading. For this reason, design of a component is the most important factor in determining a component's resistance to fatigue cracking. Common surface features that can lead to the initiation of fatigue cracks, because they act as stress concentrations, include:
 - 1. key holes on drive shafts of rotating equipment,
 - 2. mechanical notches (sharp corners or groves),
 - 3. weld joint flaws and/or mismatches,
 - 4. tool markings,
 - 5. grinding marks,
 - 6. lips on drilled holes,
 - 7. thread root notches, and
 - 8. corrosion.

In vibrating or shaking equipment, especially piping, a lack of or improperly placed support or stiffening can lead to cracks initiating at the types of stress risers or notches listed above. The normal toe or edge of a properly made, Code-acceptable weld can provide the stress concentration to initiate a fatigue crack in badly vibrating or shaking equipment. Often the cracks will form at the location(s) where the vibrating or shaking equipment is fixed and prevented from moving with the adjacent component. This situation most often needs to be addressed by reducing the amount of vibration or shaking.

- c) Metallurgical issues and microstructure.

- 1. Some materials such as titanium, carbon steel, and low-alloy steel have an "endurance limit." In such cases, the number of cycles to fatigue fracture increases with decreasing stress amplitude until a stress

amplitude endurance limit is reached below which fatigue cracking will not occur, regardless of the number of cycles.

2. For alloys with endurance limits, there is a correlation between ultimate tensile strength (UTS) and the minimum stress amplitude necessary to initiate fatigue cracking, i.e. the endurance limit. The ratio of endurance limit to UTS is typically between 0.4 and 0.5.
3. 300 series SS, 400 series SS, aluminum, and most other non-ferrous alloys have a fatigue characteristic that does not exhibit an endurance limit. This means that fatigue fracture can be achieved under cyclic loading eventually, given enough cycles, regardless of stress amplitude. Maximum cyclic stress amplitude for design is selected by determining the cyclic stress necessary to cause fracture in the number of cycles the component needs to withstand in its lifetime. This is typically 10^6 to 10^7 cycles.
4. The endurance limit described in Item 1 above primarily applies to smooth bars and similar configurations as might be found in a pump shaft. For welded components, such as piping or other situations where inherent discontinuities, flaws, or other high stress concentrations exist, the crack initiation portion of fatigue life is essentially eliminated, leaving only the crack growth portion. This situation effectively eliminates the existence of the endurance limit. Thus, the concept of the endurance limit generally cannot be taken advantage of with vibrating or shaking equipment.
5. Inclusions found in metal can have an accelerating effect on fatigue cracking. This is of importance when dealing with older, "dirty" steels or weldments, as these often have inclusions and discontinuities that can degrade fatigue resistance.
6. Heat treatment can have an effect on fatigue resistance of a metal. In general, finer-grained microstructures tend to perform better than coarse grained. Heat treatments such as quenching and tempering can improve fatigue resistance of carbon and low-alloy steels.

3.43.4 Affected Units or Equipment

- a) Socket welds and small-bore piping (e.g. bypass lines, minimum flow loops) associated with or near pumps, compressors, or other rotating or reciprocating equipment that are not properly gusseted and supported.
- b) Small branch connections with unsupported valves or controllers that may see vibration from adjacent equipment and/or wind. For small components, resonance can also produce a cyclic load and should be taken into consideration during design and reviewed for potential problems after installation.
- c) Safety-relief valves that are subject to chatter, premature pop-off, fretting, and failure to operate properly.
- d) High-pressure-drop control valves or steam-reducing stations that can cause serious vibration problems in connected piping.
- e) Rotating shafts on centrifugal pumps and compressors that have stress concentrations due to changes in radii and keyways.
- f) Heat exchanger tubes that may be susceptible to vortex shedding.
- g) Pressure swing absorber vessels in hydrogen purification units.
- h) Transient conditions (such as start-ups, shutdowns, upsets, etc.) can create intermittent, but severe, vibrating conditions.

3.43.5 Appearance or Morphology of Damage

- a) Damage is usually in the form of a crack emanating from a point of high stress concentration or discontinuity such as thread, a weld (Figure 3-43-1 to Figure 3-43-4), or the corner of a keyway in a shaft.

- b) The signature mark of a fatigue failure is a “clam-shell”-type fingerprint that has concentric rings called “beach marks” emanating from the crack initiation site (Figure 3-43-5 to Figure 3-43-8). This signature pattern results from the “waves” of crack propagation that occur during cycles above the threshold loading. These concentric cracks continue to propagate until the cross-sectional area is reduced to the point where failure due to tensile overload occurs.
- c) Cracks nucleating from a surface stress concentration or defect will typically result in a single “clam shell” fingerprint. (Figure 3-43-8)
- d) Cracks resulting from cyclical overstress of a component without one significant, isolated stress concentration point will typically result in a fatigue failure with multiple points of nucleation and hence multiple “clam shell” fingerprints. These multiple nucleation sites, often called “ratchet markings,” are the result of microscopic yielding that occurs when the component is momentarily cycled above its yield strength. (Figure 3-43-9)

3.43.6 Prevention/Mitigation

- a) Piping and other fixed equipment.
 - 1. The best defense against fatigue cracking is good design that helps minimize stress concentration of components that are in cyclic service.
 - 2. Fatigue cracking in piping can usually be eliminated or reduced through proper design and the use of properly placed support and vibration dampening equipment. Material upgrades are not usually a solution.
 - 3. Install gussets or stiffeners on small-bore connections so that they cannot move independently of the larger pipe or other component to which they are connected. Eliminate unnecessary connections.
 - 4. Vortex shedding can be minimized at the outlet of control valves and safety valves through proper side branch sizing and flow stabilization techniques.
 - 5. Vibration effects may be shifted when a vibrating section is anchored. Special studies may be necessary before anchors or dampeners are provided, unless the vibration is eliminated by removing the source.
 - 6. Assure good fit-up and smooth transitions for welds. Employ a gradual bore taper on the thicker component when transitioning between different pipe schedules.
 - 7. Minimize weld defects as these can accelerate fatigue cracking.
 - 8. Minimize grinding marks, nicks, and gouges on the surface of components subject to cyclic loading.
 - 9. Use low-stress stamps and marking tools.
- b) Rotating equipment.
 - 1. Allow for a generous radius along edges and corners, particularly in shaft keyways.
 - 2. Remove any burrs or lips caused by machining.
 - 3. Although fatigue cracking problems are generally addressed by design and fabrication improvements, ensure that the metal selected has fatigue life sufficient for its intended cyclic service.
- c) API 579-1/ASME FFS-1 contains useful information related to determining critical fatigue crack sizes and assessing crack growth rates.

3.43.7 Inspection and Monitoring

In high cycle fatigue, the time required for a crack to initiate or grow sufficiently to be identifiable by NDE

methods can be a majority of the fatigue life, making detection before cracking and failure difficult. For this reason, it is normally impractical to rely on NDE methods for routine, global inspection of fixed equipment to avoid fatigue cracking failures. Frequent NDE in a focused program aimed at a specific, known problem area can be used for finding cracks before failure, but this is not normally considered an effective, long-term approach to managing the problem.

- a) PT can be used to detect cracks open to the surface.
- b) MT (including WFMT) can be used to detect cracks open to the surface or near the surface.
- c) Angle beam (SWUT and PAUT) can be used to detect fatigue cracks at known or suspected areas of concern, e.g. at stress concentrations and welded connections, and where cracking is internal, i.e. initiating on the ID surface and not visible from the outside. In some situations, e.g. with very thick components, compression wave UT may be needed.
- d) Compression wave UT can detect cracking in bolts.
- e) Vibration monitoring of rotating equipment may provide online detection of conditions that can result in shaft failures due to out of balance conditions.
- f) Piping oscillation, vibration, or water hammer, especially involving small-bore components that are not adequately supported, is often visually apparent. Focus on weld joints and locations where the pipe is fixed and prevented from moving. Pipe vibrations can be measured using special monitoring equipment.
- g) Pipe supports and spring hangers should be checked on a regular schedule.
- h) Audible sounds of vibration emanating from components such as control valves can be an indication of conditions capable of causing fatigue cracks.
- i) Damaged insulation jacketing may indicate excessive vibration.

3.43.8 Related Mechanisms

Thermal fatigue (3.64) and corrosion fatigue (3.21).

3.43.9 References

1. J.M. Barsom and S.T. Rolfe, *Fracture and Fatigue Control in Structures*, American Society for Testing and Materials, West Conshohocken, PA.
2. ASTM STP1428, *Thermomechanical Fatigue Behavior of Materials*, American Society for Testing and Materials, West Conshohocken, PA.
3. ASTM MNL41, *Fracture and Fatigue Control in Structures: Applications of Fracture Mechanics*, ASM International, Materials Park, OH, 1995.
4. "Environmental Effects on Components: Commentary for ASME Section III," EPRI NP-5775, Project 1757-61, Final Report, EPRI, 1998.
5. API Recommended Practice 581, *Risk-Based Inspection Technology*, American Petroleum Institute, Washington, DC, Second Edition, 2008.
6. API 579-1/ASME FFS-1, *Fitness-For-Service*, American Petroleum Institute, Washington, DC.



Figure 3-43-1—Vibration induced fatigue of a 1-in. socket weld flange in a thermal relief system shortly after start-up.

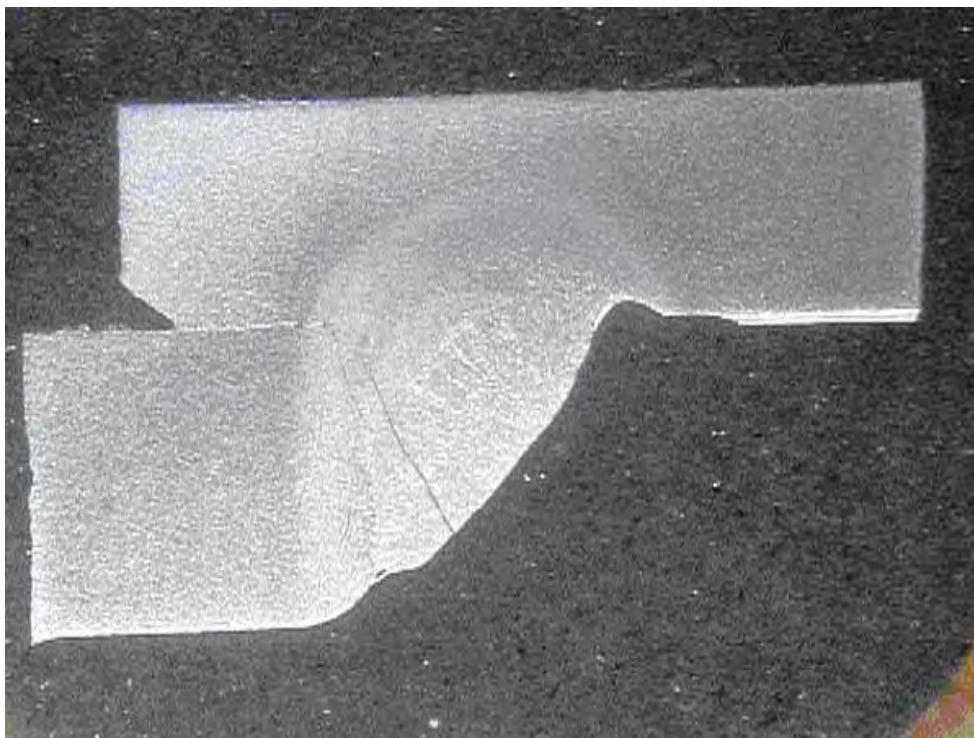


Figure 3-43-2—Cross-sectional view of the crack in the socket weld in Figure 3-41-1.

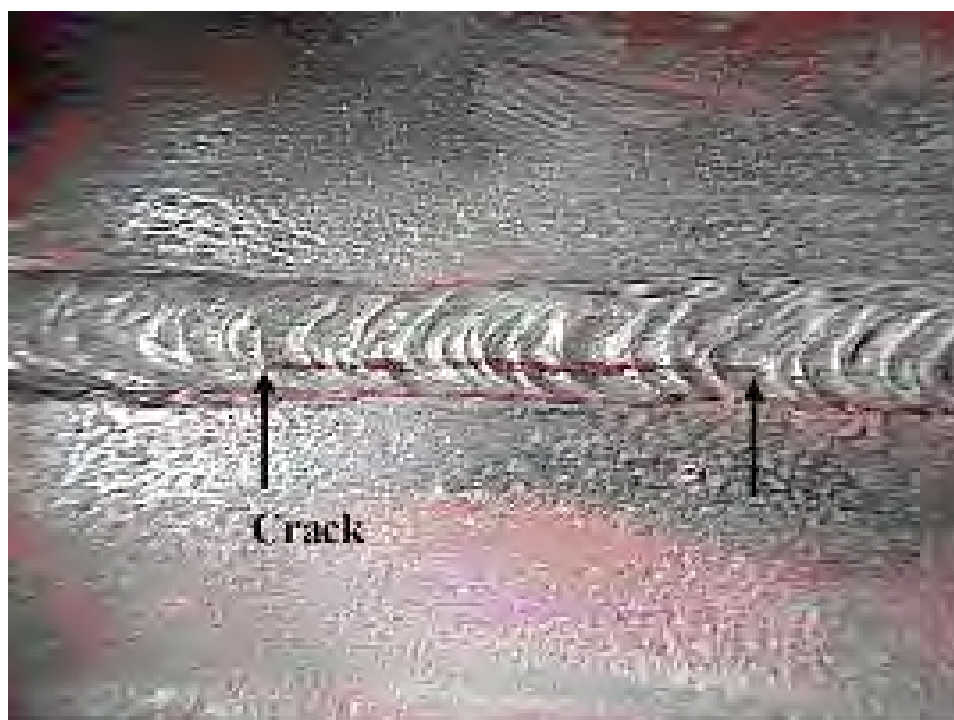


Figure 3-43-3—Fatigue crack in a 16-in. pipe-to-elbow weld in the fill line of crude oil storage tank after 50 years in service.

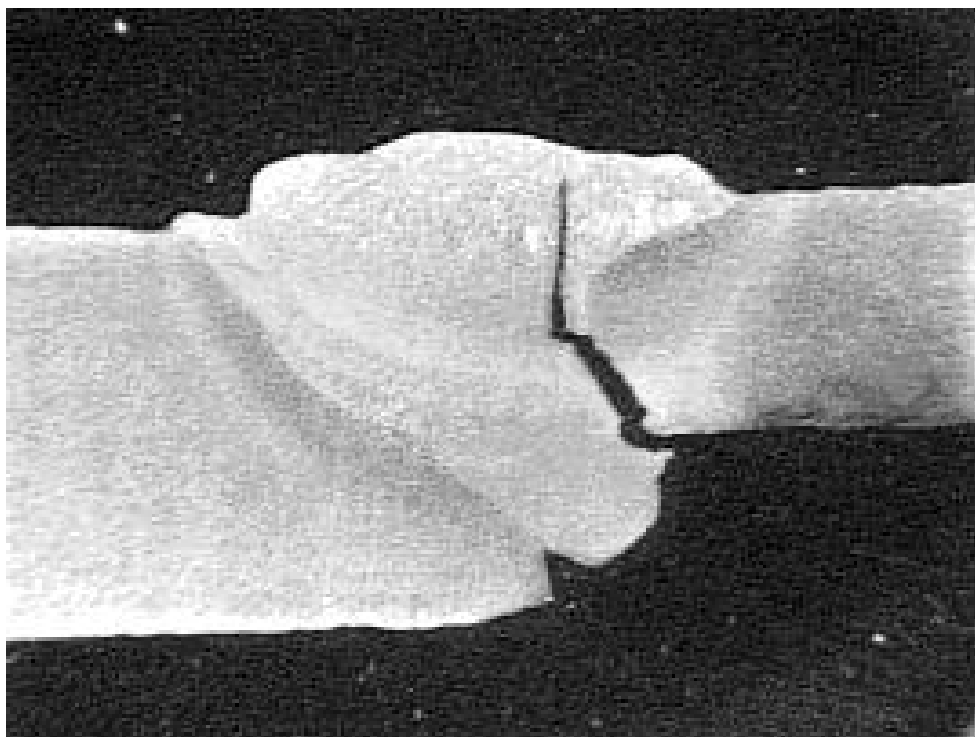


Figure 3-43-4—A cross section through the weld showing the crack location.

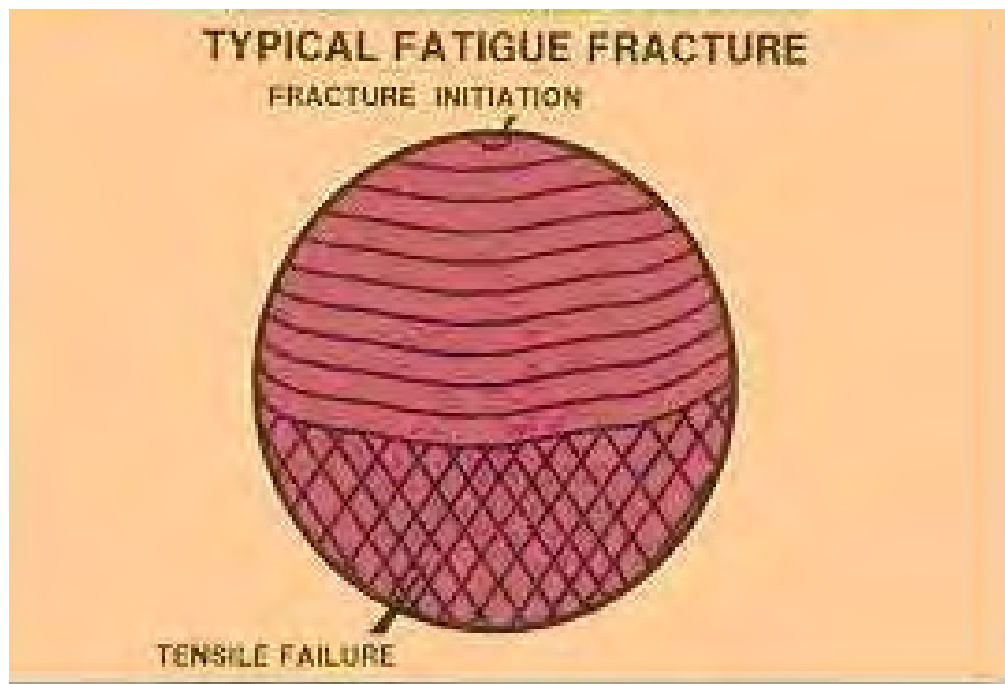


Figure 3-43-5—Schematic of a fatigue fracture surface showing “beach marks.”

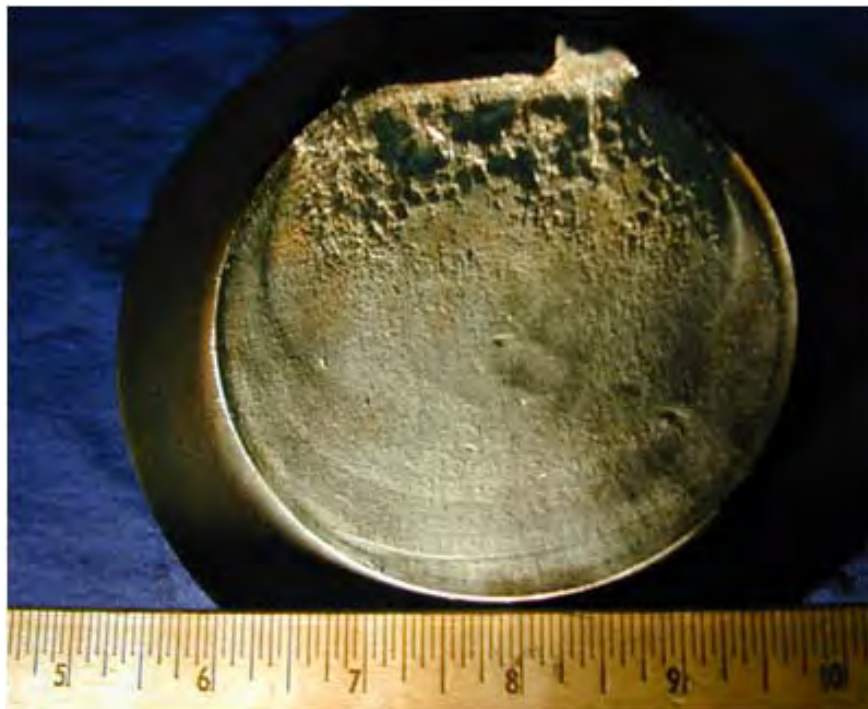


Figure 3-43-6—Compressor rod fracture surface showing “beach marks.”



Figure 3-43-7—Higher-magnification view of Figure 3-41-6 above showing “beach marks.”

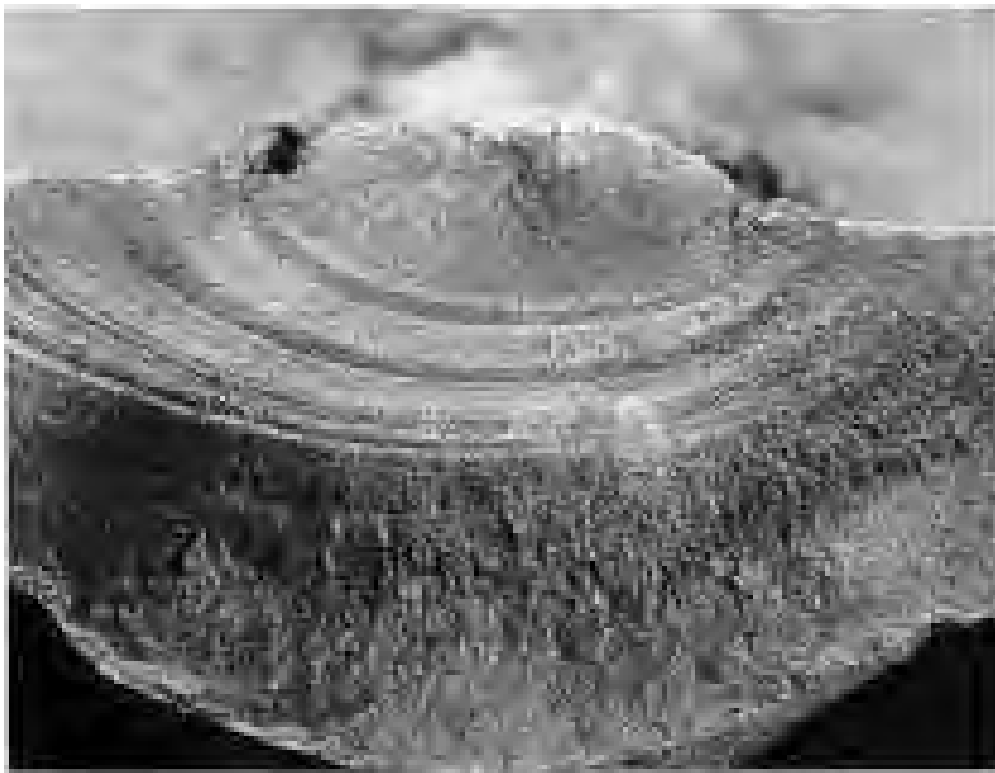


Figure 3-43-8—Fatigue fracture surface of a carbon steel pipe.

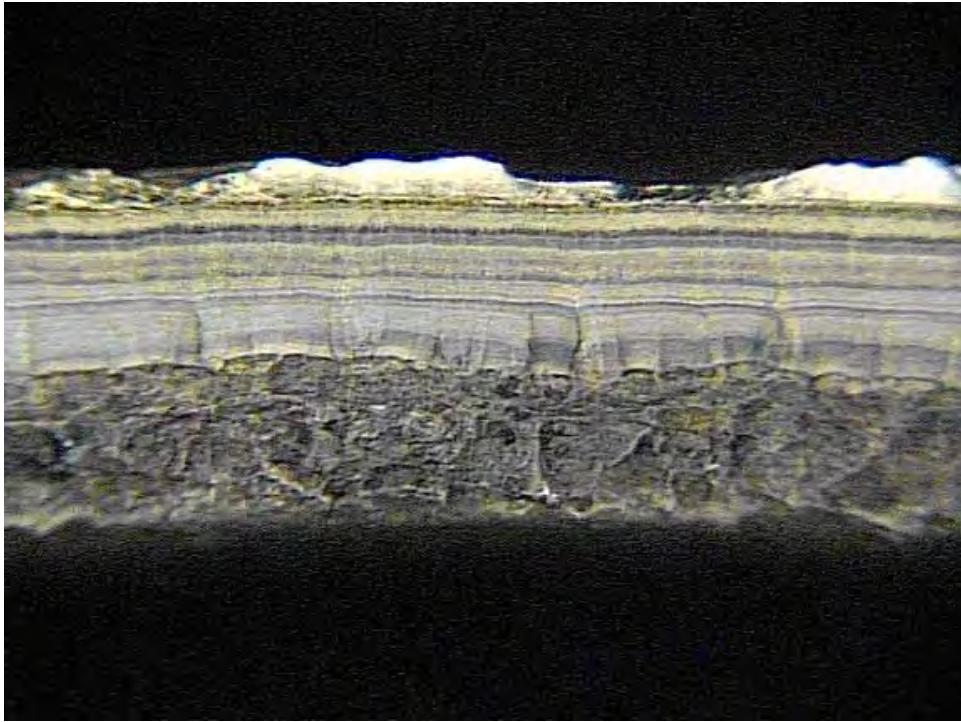


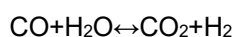
Figure 3-43-9—The surface of the fracture face of the crack shown in Figure 3-41-3 and Figure 3-41-4.

3.44 Metal Dusting

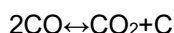
3.44.1 Description of Damage

- a) Metal dusting results in accelerated localized pitting that occurs in process streams containing carbon and oxygen. Pits form on the surface and may contain carbon soot and metal dust particles. Typically, metal dusting occurs at very high penetration rates. Penetration rates as high as 1000 mpy have been reported. It results from the following two reactions when the carbon activity is above 1.

Water Gas Shift Reaction:



Boudouard Reaction:



- b) The very high penetration rates caused by metal dusting are observed in wrought alloys where grains of metal are extracted from the surface as the grain boundaries are rapidly penetrated. In cast alloys, these same conditions result in a form of damage commonly termed “green rot.” In cast alloys, the interdendritic regions are rapidly penetrated leaving an oxide scale; however, the individual dendrites are not extracted from the surface because they are held in place due to the jagged nature of the interdendritic region.

3.44.2 Affected Materials

Low-alloy steels, 300 series SS, nickel-based alloys, and heat-resisting alloys. There is currently no known metal alloy that is immune to metal dusting under all conditions. Aluminized coatings that form a protective alumina layer on the surface have been shown to provide some protection against metal dusting.

3.44.3 Critical Factors

- a) Process stream composition, operating temperature, and alloy composition are critical factors.
- b) Metal dusting is preceded by carburization and is characterized by rapid metal wastage.
- c) Metal dusting involves a complex series of reactions that is normally found in syn gas generation processes and steam reforming heaters when conditions become reducing and the carbon activity is above 1.
- d) It usually occurs in the approximate operating temperature range of 900 °F to 1500 °F (480 °C to 815 °C). Damage increases with increasing temperature up to about 1500 °F (815 °C). Above about 1500 °F (815 °C), the calculated carbon activity for the water gas shift reaction and the Boudouard reaction will decrease to levels below 1, where metal dusting cannot occur. On the lower end of the temperature range for metal dusting, the calculated carbon activity will still be high and above 1; however, the reaction kinetics will be slow, and the metal loss will be limited.
- e) The mechanism of metal dusting is considered to involve:
1. saturation of the metal matrix by carburization;
 2. precipitation of metal carbides at the metal surface and grain boundaries;
 3. deposition of graphite from the atmosphere onto the metal carbides at the surface;
 4. decomposition of the metal carbides under the graphite and metal particles; and
 5. further deposition of graphite catalyzed by the metal particles on the surface.
- f) In high-nickel alloys, it is thought that metal dusting occurs without the formation of metal carbides.

- g) Metal dusting preferentially attacks the grain boundaries, resulting in the removal of metal grains that form what appears to be a “metal dust.”

3.44.4 Affected Units or Equipment

- a) Metal dusting occurs in processes that contain a gas composition that includes the gases shown in the water gas shift and Boudouard reactions above.
- b) Metal dusting has been reported in gas turbines, methanol reforming unit outlet piping, thermal hydrodealkylation furnaces and reactors, outlets of steam reformer heaters, and POX units.

3.44.5 Appearance or Morphology of Damage

- a) In low-alloy steels, the wastage is typically severe, and can be uniform, but usually is in the form of small pits filled with a crumbly residue of metal particles and carbon soot. There may be areas of numerous rounded pits, uniform thinning, and/or thru-wall perforations.
- b) The corrosion product is a voluminous carbon dust containing metal particles and sometimes metal oxides and carbides. Frequently, this dust will be swept away by the flowing process stream, leaving behind only the thinned or pitted metal.
- c) In stainless and high-alloy steels, the attack is frequently local, appearing as deep, round pits. ([Figure 3-44-1](#))
- d) Metallography will show that the metal is carburized under the attacked surface. ([Figure 3-44-2](#))

3.44.6 Prevention/Mitigation

- a) Sulfur in the carburizing atmosphere (usually as H_2S or a disulfide) forms a protective sulfur atmosphere on the surface that preferentially prevents carbon from being absorbed onto the surface. For protection, a low level of a reactive sulfur species such as H_2S or a disulfide must always be in the process environment. Typically, sulfur levels less than 10 ppm are needed to mitigate metal dusting. Higher sulfur levels should not be injected since it can promote sulfidation and adversely affect the activity of catalyst, if present.
- b) There is currently no known metal alloy that is immune to metal dusting under all conditions. Materials selection must be made based on the specific application and environment.
- c) In many cases, equipment is refractory lined to keep metal temperatures below the range where metal dusting occurs.
- d) An aluminum diffusion treatment (such as alonizing) applied to the base metal can be beneficial in some applications.
- e) Control of the process stream composition to ensure the carbon activity is maintained below 1 can effectively prevent metal dusting. In a steam reformer heater that is forming a syn gas, metal dusting can be prevented by maintaining the steam-to-carbon ratio of the feed above 2 to 3.

3.44.7 Inspection and Monitoring

Metal dusting normally occurs so rapidly that it is noticed only after a failure has occurred and metal loss has occurred through the wall.

- a) Metal dusting is most accurately confirmed through destructive testing, i.e. sampling for chemical or physical evidence.
- b) If internal surfaces are accessible, VT can be effective in identifying areas of severe metal wastage, including localized areas of numerous rounded pits, uniform thinning, and thru-wall perforations.
- c) RT techniques can be employed to look for pitting, cracking, and wall thinning.

- d) Filtering the cooled furnace or reactor effluent may yield metal particles that are a tell-tale indication of a metal dusting problem upstream.
- e) A specialized methodology combining intelligent pigging technology with an advanced engineering assessment has shown success in detecting and quantifying the damage mechanism.

3.44.8 Related Mechanisms

Carburization (3.13).

3.44.9 References

1. API Recommended Practice 573, *Inspection of Fired Boilers and Heaters*, American Petroleum Institute, Washington, DC.
2. H.J. Grabke, "Metal Dusting of Low- and High-alloy Steels," *CORROSION*, Vol. 51, 1995, p. 711.
3. H.J. Grabke, R. Krajak, and J.C. Nava Paz, "On the Mechanism of Catastrophic Carburization: Metal Dusting," *Corrosion Science*, Vol. 35, Nos. 5–8, 1993, p. 1141.
4. B.A. Baker and G.D. Smith, "Metal Dusting of Nickel-Containing Alloys," Paper No. 445, *Corrosion/98*, NACE International, Houston, TX.
5. *Corrosion Control in the Refining Industry*, NACE Course Book, NACE International, Houston, TX, 1999.
6. *Corrosion Control in the Petrochemical Industry*, ASM International, ISBN-13: 9780871705051, 1994, pp. 231–233.
7. D.H. Herring, "What to Do About Metal Dusting," *Heat Treat Progress*, 2003, pp. 20–24.
8. P.J. Van De Loo, A. Wolfert, R. Schelling, H.J. Schoorlemmer, and T.M. Kooistra, "Low-alloy Steel Metal Dusting: Detailed Analysis by Means of Acoustic Emission," *Journal of Acoustic Emission*, Vol. 20, 2002, pp. 238–247.



Figure 3-44-1—Metal dusting of a 304H stainless steel pipe.

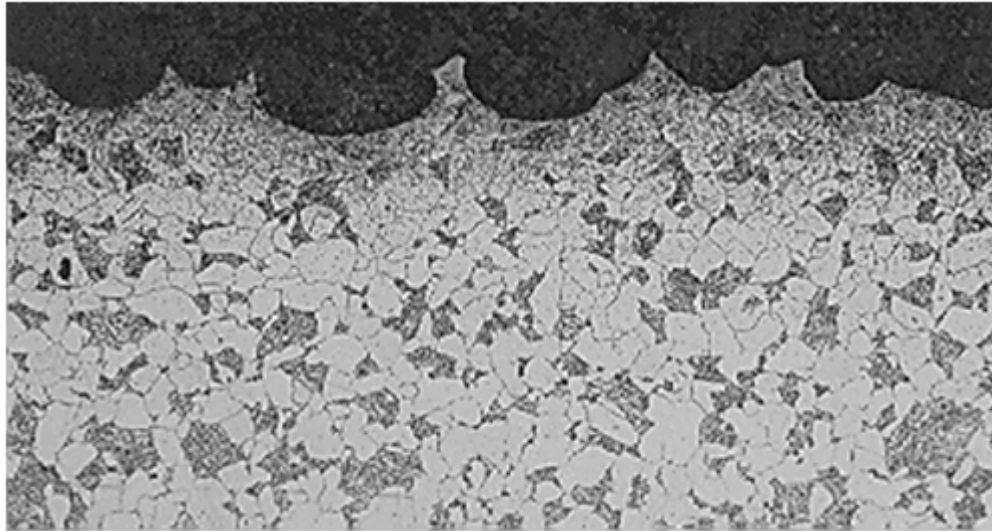


Figure 3-44-2—Carbon steel separator plate in a natural gas preheater showing classical pattern of carburization and pitting.

3.45 Microbiologically Influenced Corrosion

3.45.1 Description of Damage

Corrosion caused by living organisms such as bacteria, algae, or fungi. It is often associated with the presence of tubercles or slimy organic substances. Often, the bacteria produce localized corrosion in the form of pitting or crevice corrosion.

3.45.2 Affected Materials

Most common materials of construction including carbon and alloy steels, 300 series SS and 400 series SS, aluminum alloys, copper alloys, and some nickel alloys. Titanium appears to be highly resistant.

3.45.3 Critical Factors

- a) Microbiologically influenced corrosion (MIC) is found in aqueous environments. Occasionally it is found in services where water is intermittently present. Stagnant or low-flow conditions allow and/or promote the growth of microorganisms.
- b) Because there are many types, organisms can survive and grow under a wide range of conditions including lack of oxygen, light or dark, high salinity, pH range of 0 to 12, and temperatures from 0 °F to 235 °F (–15 °C to 115 °C).
- c) Systems may become “inoculated” by the introduction of organisms that multiply and spread unless controlled.
- d) Different organisms thrive on different nutrients including inorganic substances (e.g. sulfur, ammonia, iron, sulfate compounds, and H₂S) and organic substances (e.g. hydrocarbons and organic acids). In addition, all organisms require a source of carbon, nitrogen, and phosphorous for growth. Corrosion is often blamed on iron-oxidizing bacteria or SRB. However, these organisms are typically only part of a complex colony of multiple types of interdependent organisms, each capable of creating by-products that might be a food source for others.
- e) In-leakage of process contaminants such as hydrocarbons or H₂S may lead to a massive increase in biofouling and corrosion.

3.45.4 Affected Units or Equipment

- a) MIC is often found in water-cooled heat exchangers, in the bottom water layer of storage tanks, in piping with stagnant or low flow, and in piping in contact with some soils.
 - 1. Product storage tanks and water-cooled heat exchangers in any unit where cooling water is not properly treated can be affected.
 - 2. Stagnant process lines with trapped water can suffer from MIC.
- b) Drain systems and other water-containing systems associated with docks and ship loading/unloading facilities can experience MIC.
- c) MIC is commonly found in equipment where the hydrotest water has not been removed or where equipment has been left outside and unprotected. 300 series SS are often affected unless precautionary measures are taken.
- d) Fire-water systems can be affected.

3.45.5 Appearance or Morphology of Damage

- a) MIC corrosion is frequently observed as localized pitting under deposits or tubercles that shield the organisms. Tubercles also form on carbon steel exposed to oxygenated water, so the presence of tubercles is not a guarantee of MIC.
- b) Damage is often characterized by cup-shaped pits within pits (the halo effect) in carbon steel or subsurface cavities in stainless steel. (Figure 3-45-1 to Figure 3-45-7) However, these pits are often indistinguishable from under-deposit corrosion in carbon steel and chloride pitting in stainless steels. Pit morphology alone may not be a reliable indicator of the cause of corrosion.

3.45.6 Prevention/Mitigation

- a) Microbes require water to thrive. Systems that contain water (cooling water, storage tanks, etc.) should be treated with biocides such as chlorine, bromine, ozone, ultraviolet light, or proprietary compounds. Often, multiple biocides are needed to keep the levels of bacteria in the appropriate ranges.
- b) Proper application of biocides will control, but not eliminate, microbes; therefore, continued treatment is often necessary.
- c) Periodically flushing and cleaning susceptible systems will help minimize colony growth and resultant MIC.
- d) Minimize low-flow or stagnant zones in water-containing systems. A flow rate of 3 fps (1 m/s) will inhibit colony formation and thereby minimize the likelihood of MIC.
- e) Lines should be sloped to assist in drainage.
- f) Systems that are not designed or intended for water containment should be kept clean and dry.
- g) Empty hydrotest water as soon as possible. Remove moisture and prevent additional moisture intrusion.
- h) Coating and cathodically protecting underground structures and interiors of storage tanks have been shown to be effective mitigation methods for MIC.
- i) Biocides are generally not effective in a system that is already contaminated with colonies protected by a sludge layer. Effective mitigation of established organisms requires complete removal of deposits and organisms, typically using some combination of pigging, blasting, chemical cleaning, and biocide treatment.

3.45.7 Inspection and Monitoring

- a) In cooling water systems, effectiveness of treatment is monitored by measuring biocide residual, microbe counts, and visual appearance of the water. Sampling and analysis can be performed to better understand the bacteria population (e.g. ATP, qPCR). While effective treatment and monitoring are key to identifying the potential for MIC, it still can occur in areas with stagnant flow. Also, the type of microorganisms being investigated should be identified to ensure proper incubation of water samples (e.g. using an appropriate temperature for incubation for thermophilic bacteria).
- b) Special probes have been designed to monitor for evidence of fouling that may precede or coincide with MIC damage. Corrosion coupons can be used to identify MIC by sampling the coupon surface after it is pulled from service; however, it should be noted that just because sessile bacteria populations are not found on the coupon, it does not mean they do not exist in the system.
- c) An increase in the loss of duty of a heat exchanger may be indicative of fouling and potential MIC damage. RFT can be performed to gauge depth of corrosion on heat exchanger tubes.
- d) Foul smelling water may indicate biological activity.

- e) MIC is often highly localized, so a technique that can find localized corrosion should be chosen, as applicable to the circumstances (e.g. VT, AUT, or RT).

3.45.8 Related Mechanisms

Cooling water corrosion (3.20), brine corrosion (3.10), oxygenated water corrosion (3.49), and concentration cell corrosion (3.19).

3.45.9 References

1. D.H. Pope and J.G. Stoecker, "Microbiologically Influenced Corrosion," *Process Industries Corrosion—The Theory and Practice*, NACE International, Houston, TX, 1986, pp. 227–242.
2. T.J. Tvedt, Jr., "Cooling Water Systems," *Corrosion Control in the Refining Industry*, NACE Course Book, NACE International, Houston, TX, 1999.
3. S.C. Dexter, "Biologically Induced Corrosion," *NACE Proceedings of the International Conference on Biologically Induced Corrosion, June 10–12, 1985*, NACE International, Houston, TX.
4. B.J. Little and J.S. Lee, *Microbiologically Influenced Corrosion*, John Wiley & Sons, 2007.
5. NACE TM0194, *Field Monitoring of Bacterial Growth in Oil and Gas Systems*, NACE International, Houston, TX.



Figure 3-45-1—MIC on a diesel tank bottom.

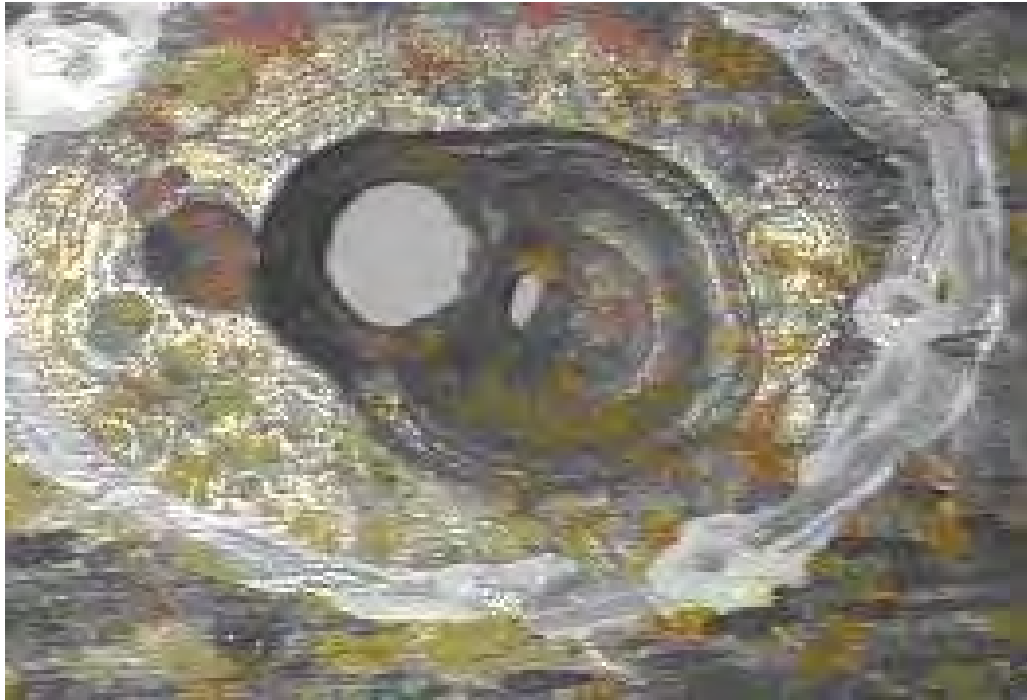


Figure 3-45-2—Pitting corrosion on the ID of a 6-in. carbon steel sour crude line after 2½ years of service. Pits are approximately 1-in. to 2-in. wide. Note the halo effect in Figure 3-43-3.

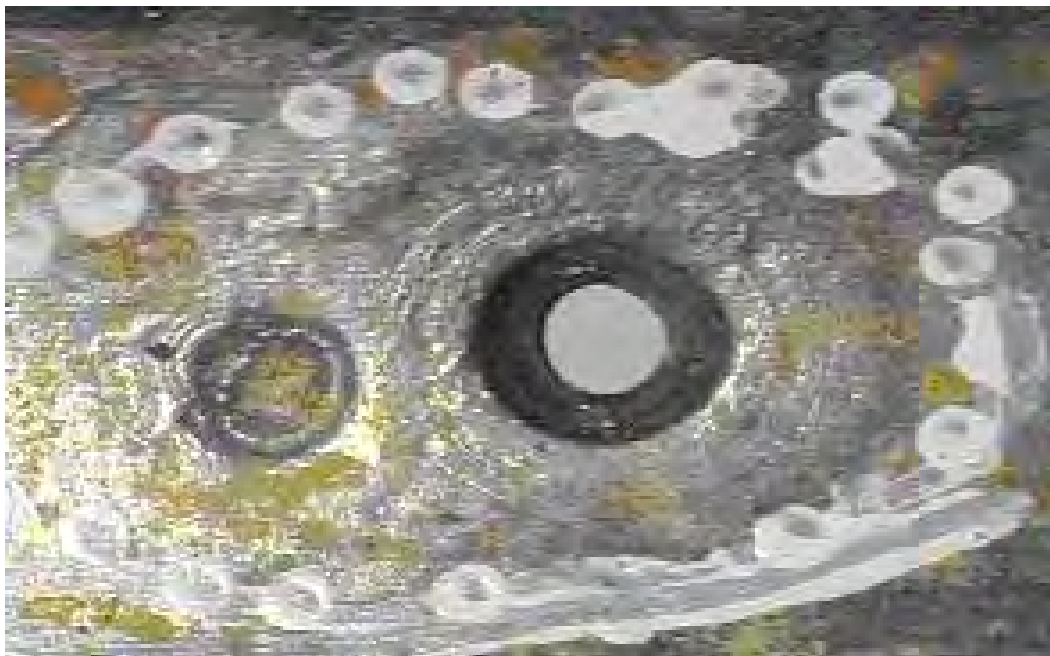


Figure 3-45-3—Same pipe as Figure 3-43-2. Note the halo effect.

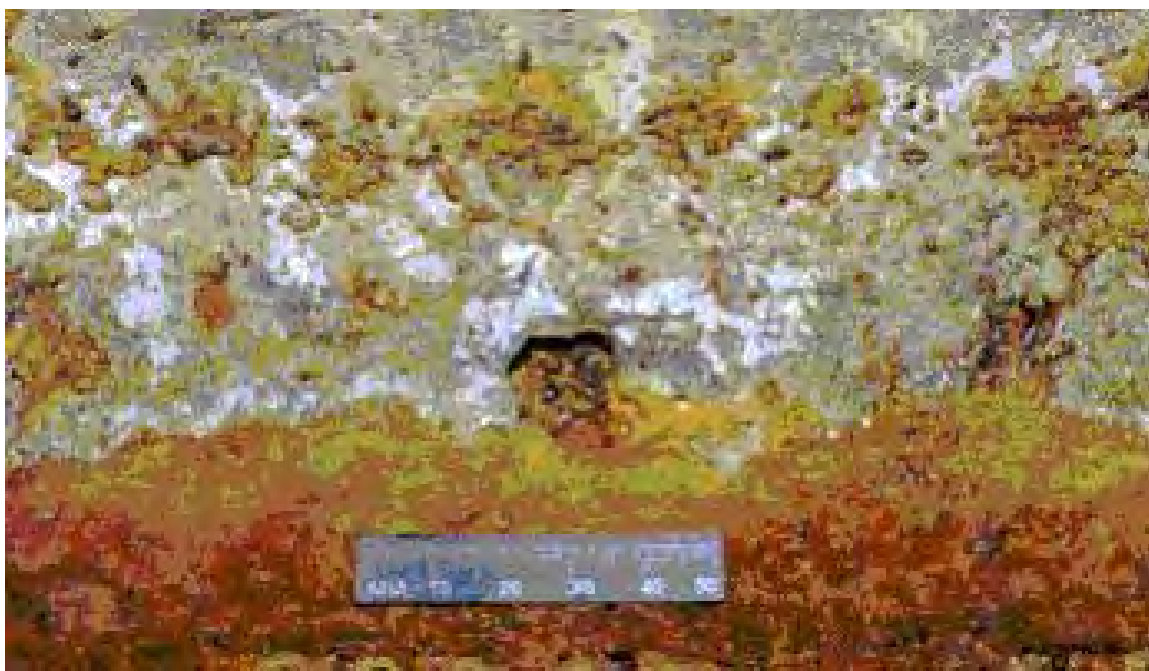


Figure 3-45-4—Oil line with MIC damage beneath tubercles.



Figure 3-45-5—Same oil line as Figure 3-43-4. Hemispherical pitting typical of MIC can be seen after grit blasting to remove the scale.

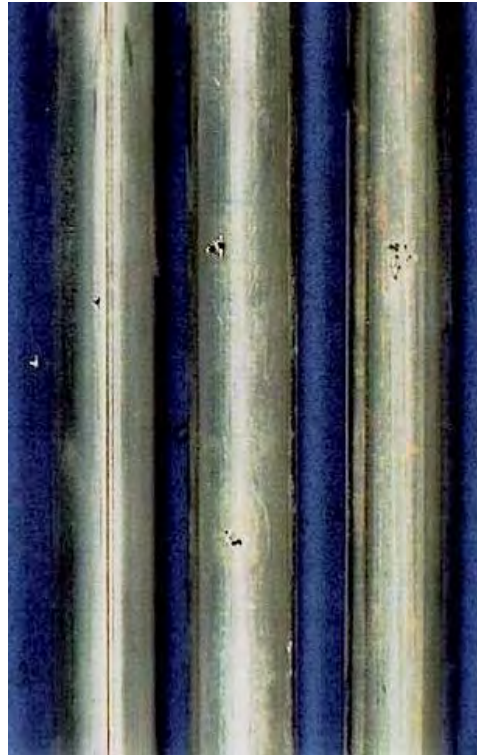


Figure 3-45-6—Type 304 stainless steel exchanger tubes failed from pitting corrosion on the shell side in cooling water service after 2½ years without biocide treatment.



Figure 3-45-7—A cross section of the tube in Figure 3-43-6 revealing severe subsurface tunneling, typical of MIC.

3.46 Naphthenic Acid Corrosion

3.46.1 Description of Damage

A form of high-temperature corrosion that occurs primarily in crude and vacuum units caused by organic naphthenic acids in the crude oil, as well as downstream units that process certain fractions or cuts that contain naphthenic acids.

3.46.2 Affected Materials

Carbon steel, low-alloy steels, 400 series SS, 300 series SS, and nickel-based alloys. See [Table 3-46-1](#).

3.46.3 Critical Factors

- a) Naphthenic acid corrosion (NAC) is a function of the naphthenic acid content, temperature, sulfur content, velocity (wall shear stress), and alloy composition.
- b) Severity of corrosion increases with increasing acidity of the hydrocarbon phase.
- c) Neutralization number or TAN is a measure of the acidity (organic acid content) as determined by various test methods such as ASTM D664. However, NAC occurs in hot dry hydrocarbon streams that do not contain a free water phase.
- d) The TAN of the crude may be misleading, because the correlation between whole crude TAN and corrosion rate is poor, especially when comparing different crudes. A high TAN crude may be less corrosive than a moderate or low TAN crude. This is because this family of organic acids that together are referred to as naphthenic acid, has a range of boiling points and tends to concentrate in various cuts. Therefore, the occurrence and severity of NAC are determined by the naphthenic acids present in the actual stream, not the crude charge. Additional factors are the following.
 1. TAN is a measure of the total amount of all acids in the crude, not just naphthenic acids.
 2. The various acids that comprise the naphthenic acid family can have distinctly different corrosivity.
 3. The structure and molecular weight of the specific naphthenic acids present have a strong impact on corrosivity, but they are not determined by TAN measurements.
- e) No widely accepted prediction methods have been developed to correlate corrosion rate with the various factors influencing it.
- f) Sulfur promotes iron sulfide formation and has an inhibiting effect on NAC, up to a point.
- g) Naphthenic acids remove protective iron sulfide scales on the surface of metals.
- h) NAC can be a particular problem with very low sulfur crudes. While a crude TAN threshold of 0.30 is typically cited as the TAN level below which NAC is not expected, some NAC cases have been reported with low sulfur and crude TAN as low as 0.10.
- i) NAC primarily occurs in hot streams above 425 °F (220 °C) but has been reported as low as 350 °F (175 °C). Severity increases with temperature up to about 750 °F (400 °C); however, NAC has been observed in hot coker gas oil streams up to 800 °F (425 °C).
- j) Naphthenic acids are destroyed by catalytic reactions in downstream hydroprocessing and FCC units. NAC of 300 series SS is also inhibited by injection of hydrogen in the feed to hydroprocessing units.
- k) Alloys containing increasing amounts of molybdenum show improved resistance to NAC. While alloys with a minimum of 2 % Mo, e.g. Types 316 and 316L SS, have demonstrated adequate resistance in some applications, it is generally agreed based on industry experience that alloys with a minimum of 3 % Mo, e.g.

Types 317 and 317L SS, are needed avoid NAC. To provide a greater degree of assurance, alloys with a minimum of 4 % Mo, e.g. Type 317LM, are sometimes selected. Under severe conditions or for components with nil corrosion allowance, 6 % Mo stainless steels and Alloy 625 have been used.

- l) Corrosion is most severe in two-phase (liquid and vapor) flow, in areas of high velocity or turbulence, and in distillation towers where hot vapors condense to form liquid phase droplets.
 - 1. For piping, NAC typically occurs in high-velocity and turbulent areas. The vapor space may be more susceptible to corrosion when flow is two phase due to acid condensation.

3.46.4 Affected Units or Equipment

- a) Crude and vacuum heater tubes, crude and vacuum heater transfer lines, vacuum bottoms piping, atmospheric gas oil (AGO) circuits, and heavy vacuum gas oil (HVGO) and sometimes light vacuum gas oil (LVGO) circuits. NAC has also been found in resid transfer lines from the vacuum unit to the coker. Although thermal cracking in the delayed coker is thought to break down naphthenic acids, making NAC uncommon in coker units, NAC has been reported in the light coker gas oil (LCGO) and heavy coker gas oil (HCGO) streams in delayed coking units processing high TAN feed.
- b) Piping systems are particularly susceptible in areas of high velocity, turbulence, or change of flow direction. Examples include pump internals, valves, elbows, tees, and reducers as well as areas of flow disturbance such as weld beads and thermowells.
- c) Crude and vacuum tower internals may also be corroded in the flash zones and packing and internals may corrode where high-acid streams condense or high-velocity droplets impinge.
- d) NAC may be found in hot hydrocarbon streams in units downstream of the crude and vacuum units, upstream of any hydrogen mix points.

3.46.5 Appearance or Morphology of Damage

- a) NAC is characterized by localized corrosion, pitting corrosion, or flow-induced grooving in high-velocity areas. (Figure 3-46-1 and Figure 3-46-2)
- b) In low-velocity condensing conditions, many alloys including carbon steel, low-alloy steels, and 400 series SS may show uniform loss in thickness and/or pitting.
- c) At temperatures below ~450 °F (230 °C), NAC can have a smoother, more uniform appearance than is typical at higher temperatures.

3.46.6 Prevention/Mitigation

- a) For units and/or components of systems that have not been designed for resistance to NAC, the options are to change or blend crudes, upgrade to a resistant alloy, utilize chemical inhibitors, or some combination thereof.
 - 1. NAC can be reduced by blending crude to reduce the TAN and/or increase the sulfur content.
- b) Monitor TAN and sulfur content of the crude charge and side streams to determine the distribution of acids in the various cuts.
- c) Use alloys with higher molybdenum content for improved resistance. Type 317L SS or other alloys with higher molybdenum content may be required.
- d) High-temperature NAC inhibitors have been used with moderate success in reducing corrosion rates. However, their potential detrimental effects on downstream catalyst activity must be considered. Phosphorus-based inhibitors tend to be more effective but have more detrimental effect on downstream catalyst than sulfur-based inhibitors. Inhibitors effectiveness needs to be monitored carefully.

3.46.7 Inspection and Monitoring

Localized wall loss due to NAC is difficult to predict and find.

- a) VT can be used where access is available.
- b) RT can be used to look for and identify the extent of localized wall loss.
- c) Close-grid UT thickness examination or UT thickness scanning can also be used, either as an alternative to RT, e.g. when RT is not practical due to piping size or configuration, or as a follow-up to RT.
- d) Permanently mounted thickness monitoring sensors can be used.
- e) Electrical resistance corrosion probes, hydrogen probes, and corrosion coupon racks can be used if properly located. However, caution needs to be exercised with intrusive devices such as ER probes and coupons since they may create the turbulence that results in corrosion not only of the measuring device but of the adjacent pipe wall.
- f) Streams can be monitored for Fe and Ni content to assess corrosion in the system.

3.46.8 Related Mechanisms

Sulfidation (3.61) is a competing and complimentary mechanism that must be considered in most situations with NAC. In cases where thinning is occurring, it may be difficult to distinguish between NAC and sulfidation, and both may be contributing to wall loss, but pitting damage is attributable to NAC.

3.46.9 References

1. W.A. Derungs, "Naphthenic Acid Corrosion—An Old Enemy of the Petroleum Industry," *CORROSION*, Vol. 12, No. 12, NACE International, Houston, TX, pp. 41–46.
2. J. Gutzeit, "Naphthenic Acid Corrosion," Paper No. 156, *Corrosion/76*, NACE International, Houston, TX.
3. R.L. Piehl, "Naphthenic Acid Corrosion in Crude Distillation Units," *Materials Performance*, January 1988.
4. B.E. Hopkinson and L.E. Penuela, "Naphthenic Acid Corrosion by Venezuelan Crudes," Paper No. 97502, *Corrosion/97*, NACE International, Houston, TX.
5. M.J. Nugent and J.D. Dobis, "Experience with Naphthenic Acid Corrosion in Low TAN Crudes," Paper No. 98577, *Corrosion/98*, NACE International, Houston, TX.
6. API Recommended Practice 581, *Risk-Based Inspection Methodology*, American Petroleum Institute, Washington, DC.
7. C. Shargay et al., "Survey of Materials in Hydrotreater Units Processing High Tan Feeds," Paper No. 07573, *Corrosion/2007*, NACE International, Houston, TX.

Table 3-46-1—Alloys Listed in Approximate Order of Increasing Resistance to NAC

CS, 1¼Cr-½Mo, 2¼Cr-1Mo, 5Cr-½Mo 9Cr-1Mo, 410 SS, 304L SS, 321 SS, 347 SS 316 SS (2 % to 3 % Mo) 317 SS (3 % to 4 % Mo) 6 % Mo alloys Alloy 625, Alloy 276
NOTE Alloys listed above 316 SS in the table are not considered NAC-resistant materials.



Figure 3-46-1—Erosion-corrosion damage due to NAC in a 10-in. 5Cr- $\frac{1}{2}$ Mo elbow in the outlet of a vacuum heater in a vacuum distillation unit.



Figure 3-46-2—Severe NAC of 410 SS trays and bubble caps in the HVGO section of the vacuum tower fed by the vacuum heater referred to in Figure 3-44-1.

3.47 Nitriding

3.47.1 Description of Damage

Nitriding is the formation of a hard, brittle surface layer on some alloys due to exposure to high-temperature process streams containing high levels of nitrogen compounds such ammonia or cyanides, particularly under reducing conditions. It may adversely affect corrosion resistance, creep strength, ductility and fracture toughness, and weldability.

In most cases, a harder surface layer of a vessel or component by itself will not affect its mechanical integrity. However, the concern is for cracks developing in the nitrided layer and propagating into the base metal.

Nitriding of the surface is also done as a manufacturing process to surface harden (case harden) components to provide improved abrasion and wear resistance.

3.47.2 Affected Materials

- a) Carbon steel, low-alloy steels, 400 series SS, and 300 series SS are affected.
- b) Nickel-based alloys are more resistant.

3.47.3 Critical Factors

- a) Nitriding is a diffusion-controlled process dependent on temperature, time, partial pressure of nitrogen, and metal composition.
- b) Temperatures must be high enough to allow for the thermal breakdown/dissociation of nitrogen from ammonia or other compounds and for diffusion of nitrogen into the metal. Since diffusion is a function of time, longer exposure times at elevated temperature increase the amount and depth of nitriding.
- c) Nitriding begins above 600 °F (315 °C) and becomes more rapid and severe above 900 °F (480 °C).
- d) Above 770 °F (410 °C), preferential grain boundary nitriding may lead to microcracking and embrittlement.
- e) High gas phase nitrogen activity (i.e. high partial pressure of nitrogen) promotes nitriding.
- f) Alloys containing 30 % to 80 % nickel are more resistant.

3.47.4 Affected Units or Equipment

Nitriding can occur wherever appropriate environment and temperature conditions exist, but it is fairly uncommon in refining. Nitriding has been observed in steam-methane reformers, steam-gas cracking (olefin) plants, and ammonia synthesis plants.

3.47.5 Appearance or Morphology of Damage

- a) An example of surface cracking resulting from nitriding is shown in [Figure 3-47-1](#) to [Figure 3-47-3](#).
- b) Nitriding is usually confined to the surface of most components and will have a dull, dark gray appearance. ([Figure 3-47-1](#)) However, confirmation normally requires metallography as shown in [Figure 3-47-2](#) and [Figure 3-47-3](#), which delineate the nitrided layer as well as showing the cracks within that layer.
 - 1. When nitrogen diffuses into the surface, it forms needle-like particles of iron nitrides (Fe_3N or Fe_4N) that can only be confirmed by metallography.

- c) In a more advanced stage, the material will exhibit very high surface hardness, which may be identifiable by surface hardness measurement but is readily measured by microhardness testing of metallographic samples. (Figure 3-47-3)
- d) Nitriding of low-alloy steels containing up to 12 % chromium is accompanied by an increase in volume, and the nitrided layer tends to crack and flake.
- e) 300 series SS tend to form thin, brittle layers that may crack and spall from thermal cycling or applied stress.

3.47.6 Prevention/Mitigation

Where nitriding is an issue serious enough to require a remedy, changing to a more resistant alloy with 30 % to 80 % nickel is usually necessary. It is normally not practical to modify the process conditions to reduce the nitrogen partial pressure or lower the temperature.

3.47.7 Inspection and Monitoring

Various surface inspection techniques can be used detect nitriding, particularly in the advanced stages. Destructive testing is generally required to confirm the damage mechanism and the depth of penetration.

- a) Materials exposed to nitriding conditions should be inspected thoroughly because good appearance may mask damage. A change in surface color to a dull gray may indicate nitriding.
 - 1. Cast furnace tubes exposed to nitriding flue gas may change from a rough as-cast appearance to a smooth glazed appearance due to spalling of the nitride layer.
- b) Nitriding will generally affect the entire exposed surface. Where process conditions are the same, focus inspection on areas where the external temperature would most favor nitriding.
- c) Hardness testing of the affected surfaces can help indicate nitriding, because hardness of 400 to 500 HB or higher can result. However, depending somewhat on the hardness test device used, surface hardness testing results will be a mix of the hard surface layer and the softer material beneath it and therefore may not be definitive.
- d) Nitrided layers are magnetic. 300 series SS should be checked for magnetism as an initial screening. However, some cast 300 series SS alloys are magnetic and could yield a false positive.
- e) Metallography is generally required to confirm nitriding and to determine the depth of penetration of the nitride layer.
- f) ECT may be used in some cases to detect nitriding, including prior to any crack formation.
- g) In the advanced stages of nitriding, where surface cracking may have initiated, appropriate inspection techniques include PT, MT, and angle beam UT (SWUT or PAUT).

3.47.8 Related Mechanisms

Similar mechanisms involving gas diffusion into the surface layer of the metal include carburization (3.13) and metal dusting (3.44).

3.47.9 References

- 1. *ASM Handbook—Corrosion*, Volume 13, ASM International, Materials Park, OH.
- 2. *Corrosion Basics—An Introduction*, NACE International, Houston, TX, 1984, pp. 93–94.
- 3. J. Scherzer and D.P. McArthur, “Test Shows Effects of Nitrogen Compounds on Commercial Fluid Cat Cracking Catalysts,” *Oil and Gas Journal*, Vol. 84, 1986, pp. 76–82.

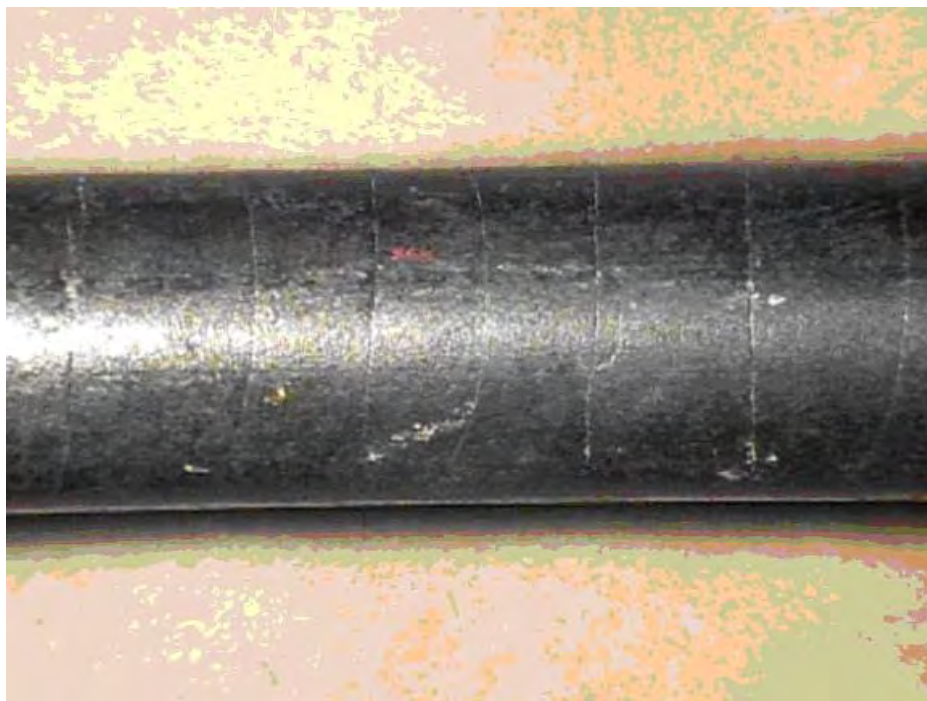


Figure 3-47-1—A nitrided 5Cr- $\frac{1}{2}$ Mo thermowell tube from an ammonia synthesis plant with surface cracking.

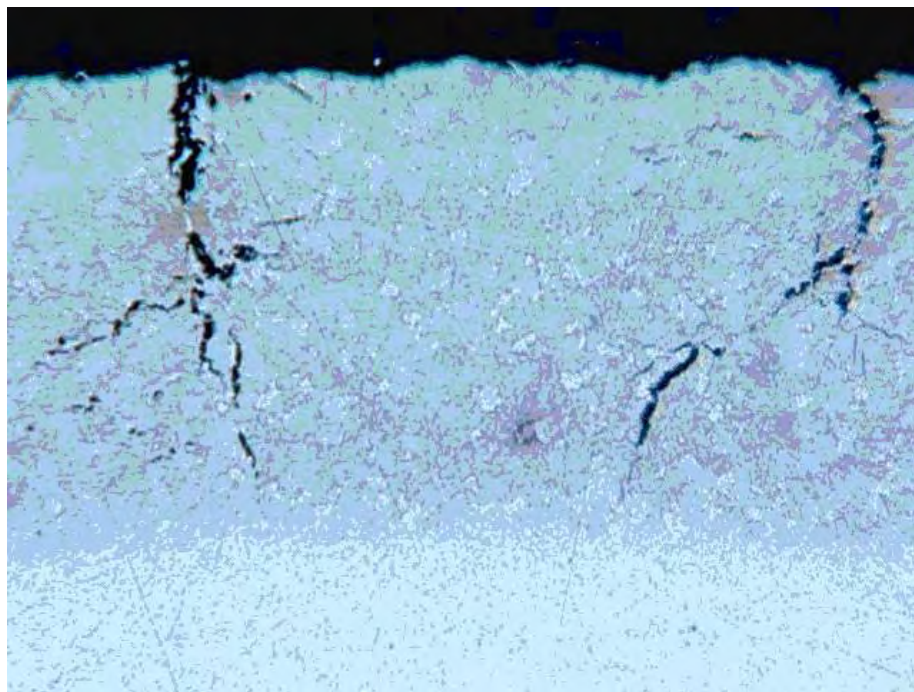


Figure 3-47-2—A photomicrograph of a cross section through the tube in Figure 3-45-1 showing the interface between the shallow nitrided layer on the surface (gray) and the unaffected base metal (white). Cracks initiated from the OD surface at the top. Magnification 50X.

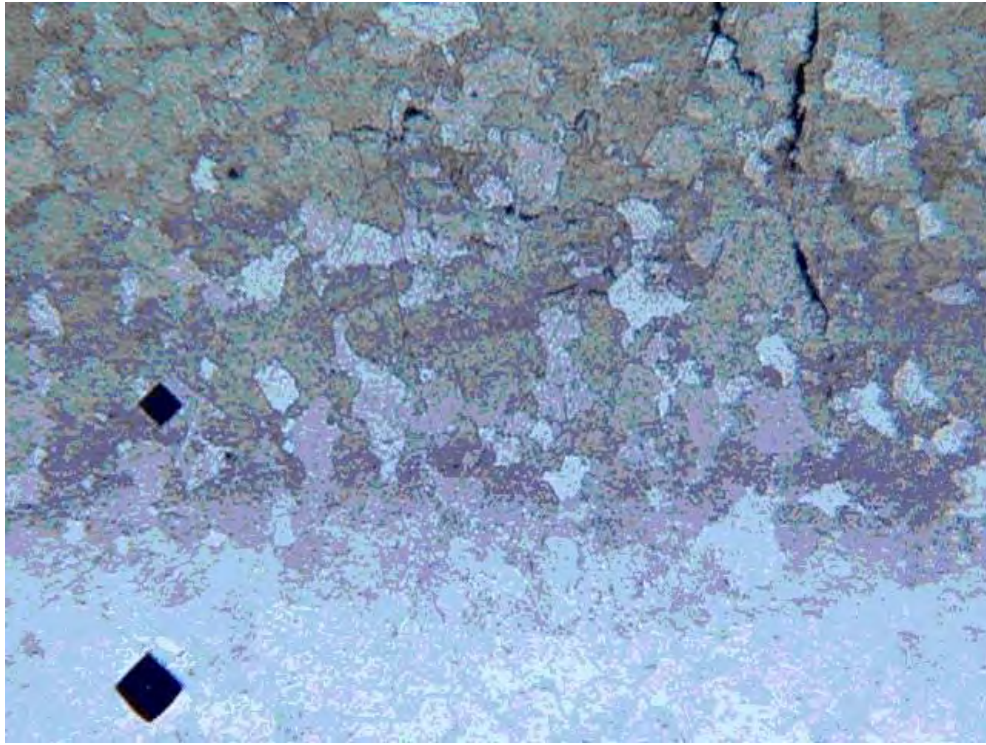


Figure 3-47-3—A higher-magnification photomicrograph of the same tube showing the smaller diamond-shaped hardness indentation in the hard nitrided layer (540 HB) vs the larger indentation in the softer base metal (210 HB). Magnification 150X.

3.48 Oxidation

3.48.1 Description of Damage

Oxygen, most often present as a component of air (approximately 21 %), reacts with carbon steel and other alloys at high temperature, converting the metal to oxide scale and thereby reducing the metal wall thickness.

3.48.2 Affected Materials

- a) All iron-based materials including carbon steel and low-alloy steels, both cast and wrought, are affected.
- b) All 300 series SS, 400 series SS, and nickel-based alloys also oxidize to varying degrees, depending on composition and temperature.

3.48.3 Critical Factors

- a) The primary factors affecting high-temperature oxidation are metal temperature and alloy composition.
- b) Oxidation of carbon steel begins to become significant above about 1000 °F (540 °C). Rates of metal loss increase with increasing temperature.
- c) In general, the resistance of carbon steel and other alloys is determined by the chromium content of the material. Increasing chromium levels produce a more protective oxide scale. The 300 series SS are resistant to scaling up to about 1500 °F (815 °C). See [Table 3-48-1a](#) and [Table 3-48-1b](#) and [Figure 3-48-1](#).
- d) The presence of water vapor can significantly accelerate oxidation rates of some steels including 9Cr-1Mo. (Reference 4)

3.48.4 Affected Units or Equipment

Significant oxidation occurs in fired heaters, boilers, and other combustion equipment, as well as piping and equipment that operate in high-temperature, oxygen-containing environments where metal temperatures exceed about 1000 °F (540 °C).

3.48.5 Appearance or Morphology of Damage

- a) Carbon steel, low-alloy steels, and 12Cr stainless steels suffer general thinning due to oxidation. Usually, the component will be covered on the outside surface with an oxide scale, depending on the temperature and exposure time. ([Figure 3-48-2](#) to [Figure 3-48-4](#)).
- b) 300 series SS and nickel alloys generally have a very thin dark scale unless exposed to extremely high temperatures where metal loss rates are excessive.

3.48.6 Prevention/Mitigation

- a) Resistance to oxidation is best achieved by upgrading to a more resistant alloy.
- b) Chromium is the primary alloying element that affects resistance to oxidation. Other alloying elements, including silicon and aluminum, are effective, but their concentrations are limited due to adverse effects on mechanical properties. They are often used in special alloys for applications such as heater supports, burner tips, and components for combustion equipment.

3.48.7 Inspection and Monitoring

- a) Process conditions should be monitored to establish trends of high-temperature equipment where oxidation can occur.
- b) Temperatures can be monitored with tube-skin thermocouples and/or infrared thermography.

- c) RT can be used to measure remaining thickness when oxidation occurs on the external surface. Alternatively, the oxide could be removed, e.g. using a flapper wheel, to allow UT measurement of the remaining wall thickness.
- d) UT can be used to measure remaining thickness when oxidation occurs on the internal surface.
- e) EMAT has been used to measure general external wall loss on heater tubes.

3.48.8 Related Mechanisms

Other high-temperature gas corrosion mechanisms are sulfidation (3.61), high-temperature H₂/H₂S corrosion (3.35), carburization (3.13), and metal dusting (3.44). Oxidation damage referred to in this section is due to surface scaling. Some damage mechanisms result in internal oxidation, which is outside the scope of this document.

3.48.9 References

1. API Recommended Practice 581, *Risk-Based Inspection Technology*, American Petroleum Institute, Washington, DC, Second Edition, 2008.
2. J. Gutzeit, R.D. Merrick, and L.R. Scharfstein, "Corrosion in Petroleum Refining and Petrochemical Operations," *Metals Handbook*, Volume 13, ASM International, Materials Park, OH, 1987, pp. 1262–1287.
3. *Corrosion Basics—An Introduction*, NACE International, Houston, TX, 1984, pp. 276–288.
4. F. Dettenwanger et al., "The Influence of Si, W and Water Vapor on the Oxidation Behavior of 9Cr Steels," Paper No. 01151, *Corrosion/2001*, NACE International, Houston, TX.

Table 3-48-1a—Estimated Oxidation Rates (mpy) (Reference 1)

Material	Maximum Metal Temperature (°F)											
	925	975	1025	1075	1125	1175	1225	1275	1325	1375	1425	1475
CS	2	4	6	9	14	22	33	48	—	—	—	—
1¼Cr	2	3	4	7	12	18	30	46	—	—	—	—
2¼Cr	1	1	2	4	9	14	24	41	—	—	—	—
5Cr	1	1	1	2	4	6	15	35	65	—	—	—
7Cr	1	1	1	1	1	2	3	6	17	37	60	—
9Cr	1	1	1	1	1	1	1	2	5	11	23	40
12Cr	1	1	1	1	1	1	1	1	3	8	15	30
304 SS	1	1	1	1	1	1	1	1	1	2	3	4
309 SS	1	1	1	1	1	1	1	1	1	1	2	3
310 SS/HK	1	1	1	1	1	1	1	1	1	1	1	2
800 H/HP	1	1	1	1	1	1	1	1	1	1	1	2
Material	Maximum Metal Temperature (°F)											
	1525	1575	1625	1675	1725	1775	1825	1875	1925	1975	2025	2075
CS	—	—	—	—	—	—	—	—	—	—	—	—
1¼Cr	—	—	—	—	—	—	—	—	—	—	—	—
2¼Cr	—	—	—	—	—	—	—	—	—	—	—	—
5Cr	—	—	—	—	—	—	—	—	—	—	—	—
7Cr	—	—	—	—	—	—	—	—	—	—	—	—
9Cr	60	—	—	—	—	—	—	—	—	—	—	—
12Cr	50	—	—	—	—	—	—	—	—	—	—	—
304 SS	6	9	13	18	25	35	48	—	—	—	—	—
309 SS	4	6	8	10	13	16	20	30	40	50	—	—
310 SS/HK	3	4	5	7	8	10	13	15	19	23	27	31
800 H/HP	3	4	6	8	10	13	17	21	27	33	41	50

Table 3-48-1b—Estimated Oxidation Rates (mm/yr) (Reference 1, converted)

Material	Maximum Metal Temperature (°C)											
	495	525	550	580	605	635	665	690	720	745	775	800
CS	0.05	0.1	0.15	0.23	0.36	0.56	0.84	1.22	—	—	—	—
1¼Cr	0.05	0.08	0.1	0.18	0.3	0.46	0.76	1.17	—	—	—	—
2¼Cr	0.03	0.03	0.05	0.1	0.23	0.36	0.61	1.04	—	—	—	—
5Cr	0.03	0.03	0.03	0.05	0.1	0.15	0.38	0.89	1.65	—	—	—
7Cr	0.03	0.03	0.03	0.03	0.03	0.05	0.08	0.15	0.43	0.94	1.52	—
9Cr	0.03	0.03	0.03	0.03	0.03	0.03	0.03	0.05	0.13	0.28	0.58	1.02
12Cr	0.03	0.03	0.03	0.03	0.03	0.03	0.03	0.03	0.08	0.2	0.38	0.76
304 SS	0.03	0.03	0.03	0.03	0.03	0.03	0.03	0.03	0.03	0.05	0.08	0.1
309 SS	0.03	0.03	0.03	0.03	0.03	0.03	0.03	0.03	0.03	0.03	0.05	0.08
310 SS/HK	0.03	0.03	0.03	0.03	0.03	0.03	0.03	0.03	0.03	0.03	0.03	0.05
800 H/HP	0.03	0.03	0.03	0.03	0.03	0.03	0.03	0.03	0.03	0.03	0.03	0.05
Material	Maximum Metal Temperature (°C)											
	830	855	885	915	940	970	995	1025	1050	1080	1105	1135
CS	—	—	—	—	—	—	—	—	—	—	—	—
1¼Cr	—	—	—	—	—	—	—	—	—	—	—	—
2¼Cr	—	—	—	—	—	—	—	—	—	—	—	—
5Cr	—	—	—	—	—	—	—	—	—	—	—	—
7Cr	—	—	—	—	—	—	—	—	—	—	—	—
9Cr	1.52	—	—	—	—	—	—	—	—	—	—	—
12Cr	1.27	—	—	—	—	—	—	—	—	—	—	—
304 SS	0.15	0.23	0.33	0.46	0.64	0.89	1.22	—	—	—	—	—
309 SS	0.10	0.15	0.20	0.25	0.33	0.41	0.51	0.76	1.02	1.27	—	—
310 SS/HK	0.08	0.10	0.13	0.18	0.20	0.25	0.33	0.38	0.48	0.58	0.69	0.79
800 H/HP	0.08	0.10	0.15	0.20	0.25	0.33	0.43	0.53	0.69	0.84	1.04	1.27

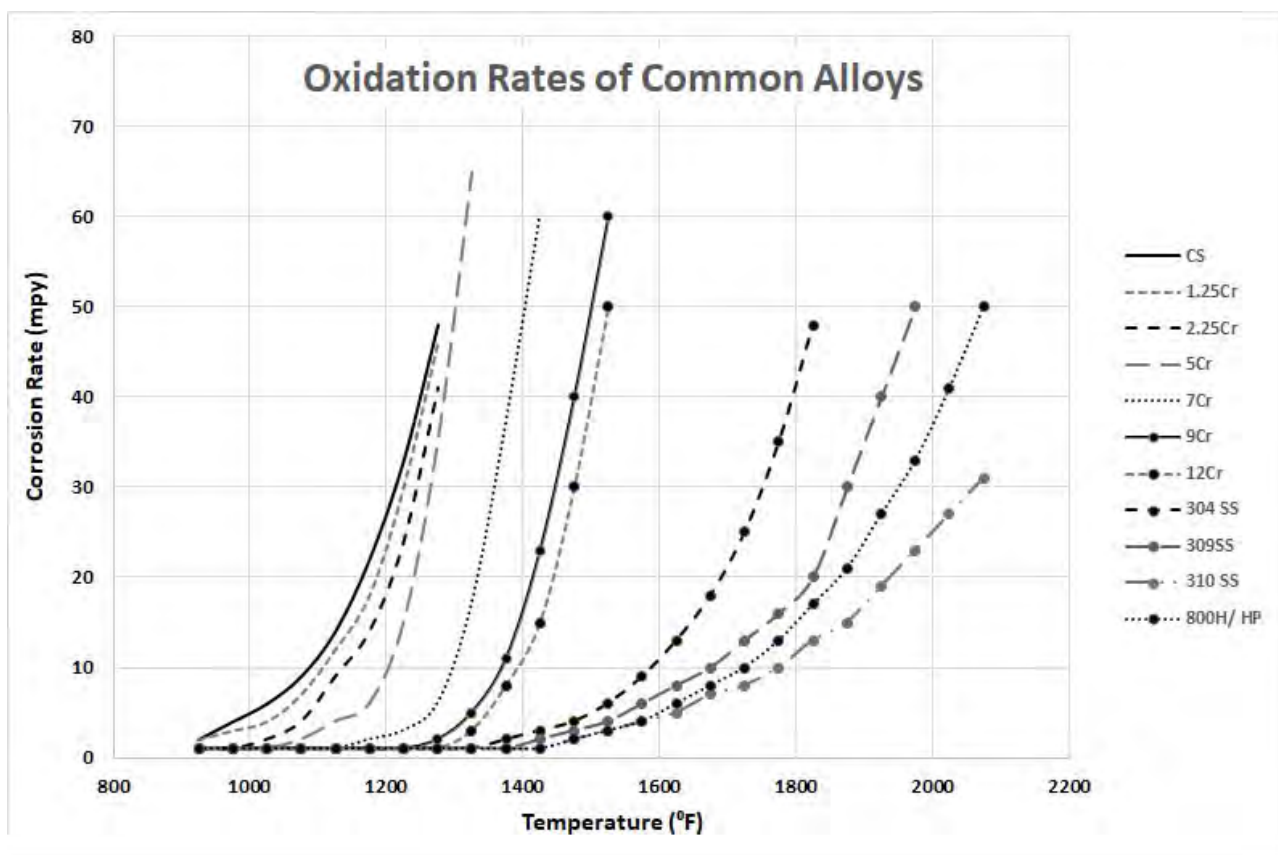


Figure 3-48-1—Estimated oxidation rates based on the data in Table 3-46-1a.

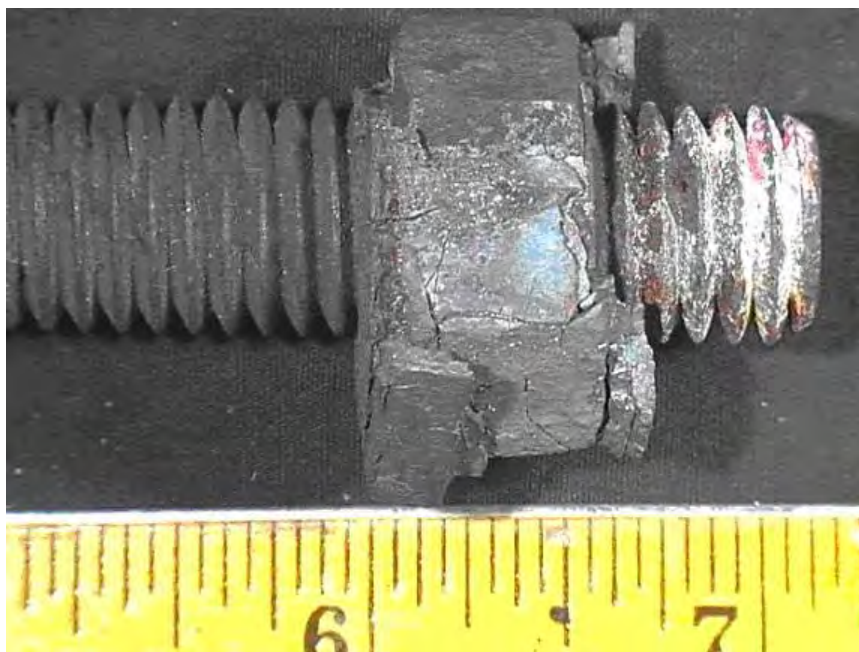


Figure 3-48-2—Oxidation of a carbon steel nut on a stainless steel stud at 1300 °F (705 °C).

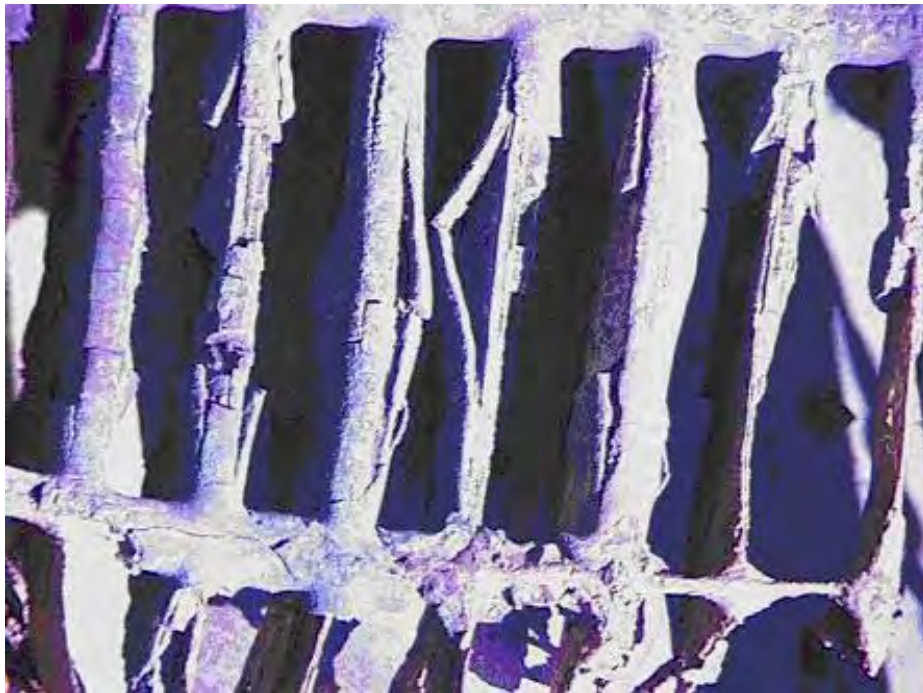


Figure 3-48-3—Oxidation of a carbon steel grid from a sulfur reactor.



Figure 3-48-4—Oxidation of the OD of a carbon steel furnace transfer line.

3.49 Oxygenated Process Water Corrosion

3.49.1 Description of Damage

The presence of oxygen-containing water in refining process streams can significantly increase corrosion activity. Because the solubility of oxygen increases as the temperature of the water decreases, the corrosion activity due to oxygen-containing water tends to be higher at lower temperatures.

3.49.2 Affected Materials

Carbon steel and low-alloy steels.

3.49.3 Critical Factors

- a) Water has to be present as a liquid phase, so the process temperature and pressure must allow for liquid water to be present. Given the presence of water, the critical factors are oxygen solubility and content, temperature, and velocity and turbulence.
- b) Oxygen solubility and content.
 - 1. Only trace levels (about 20 ppb) of oxygen are needed to significantly increase corrosion rates, and if the O_2 partial pressure in the vapor phase increases (e.g. due to more air getting into the vapor phase and thereby increasing the concentration of oxygen in the vapor phase), so does the concentration of oxygen in the water phase. As long as there is a vapor phase in the system, a higher system pressure will force more oxygen to dissolve into the water, which drives up corrosion activity.
 - 2. Fouling tends to increase, because the formation of Fe_3O_4 and other iron oxide compounds are promoted with O_2 in the system.
- c) Temperature.
 - 1. Water is more likely to exist as a liquid in lower-temperature process streams. Therefore, oxygenated water corrosion tends to be prevalent in cooler services.
 - 2. Water has a higher solubility for oxygen at lower temperature, so higher levels of oxygen can dissolve into cooler water. The greater oxygen content leads to increased corrosion rates. Corrosion rates generally increase with temperature, but in this case, as the temperature increases, the solubility of oxygen in the water decreases, thus offsetting the effect of temperature.
- d) High velocity and turbulence.
 - 1. When velocity increases beyond 10 fps (3 m/s) and/or turbulence increases, non-boiler oxygen pitting and corrosion increase. Interference with the formation of protective iron oxides promotes corrosion on fresh metal surfaces.

3.49.4 Affected Units or Equipment

- a) If a separate water phase is present, oxygenated water corrosion is typically found along the bottom of the piping system.
- b) In a system that is only water wetted, oxygenated water corrosion is typically found along the top of the piping system if localized condensation is occurring.
- c) Any turbulent areas immediately downstream of weld protrusions, piping misalignment, elbows, and penetrations in the piping can experience accelerated corrosion. If flow is two phase, more aggressive

corrosion may occur in the vapor space as the velocity of the vapor is typically higher than the velocity of the liquid.

1. Preferential weld corrosion may occur in some welds.
- d) Small-bore connections that are exposed to low or no flow and are in wetted service with O₂ present may experience oxygenated water corrosion. Vents at a water/vapor interface (if one exists) and drains that extend beyond insulation and create a cooling fin are particularly vulnerable.
 - e) Vacuum units are subject to oxygenated water corrosion because O₂ enters vacuum unit systems through leaking valve packing, flanges, seals, or undetected thru-wall corrosion. Only small amounts of O₂ are required for a significant increase in oxygenated water pitting rates. The highest corrosion rates are in vacuum systems that use steam ejectors to produce the vacuum. Oxygenated water corrosion can be found where steam condenses in the ejector coolers, in the SW system, and at the interface in the piping and exchanger shells.
 - f) O₂ that makes it through the vacuum system can potentially end up in downstream light ends units, including the flare gas recovery unit. Oxygenated water corrosion appears in any location where water may accumulate, such as compressor inlet piping low points and the piping off suction knockout drums.

3.49.5 Appearance or Morphology of Damage

Oxygenated water corrosion appears as extensive general pitting on wetted surfaces. Localized pitting occurs in low-velocity areas at reduced temperatures. If high velocities [≥ 10 fps (>3 m/s)] are an issue, localized accelerated corrosion appears where Fe₃O₄ is absent, at the back side of elbows, or where turbulence may occur, such as downstream of valves.

3.49.6 Prevention/Mitigation

- a) The key to avoiding oxygenated water corrosion is to limit the amount of O₂ within the non-aerated systems. Keeping O₂ out of the system reduces corrosion rates dramatically. If O₂ enters the system, expect corrosion activity to significantly increase. Decreasing the amount of O₂ in the system can be achieved by limiting in-leakage of air through the sources described above in 3.49.4.
 1. When O₂ concentration below 20 ppb is achieved, carbon and low-alloy steels are the preferred material.
 2. The use of oxygen scavenger injection can also be considered for non-aerated systems to reduce O₂ concentration. However, this is generally not recommended unless vacuum leaks cannot be eliminated.
- b) A filming amine corrosion inhibitor can be added to reduce corrosion in non-aerated systems. It is important to ensure the filming amine selected does not have an adverse effect on the process. Note that the overall effectiveness of the inhibitor should be proven through subsequent inspection and monitoring. Using inhibitors is generally not recommended unless vacuum leaks cannot be eliminated.
- c) Use internal vessel coatings to limit the damage from oxygenated water corrosion. The coating system needs to be designed for the service and the system in which the coating is to be applied. The temperature guidelines for the specific coating need to be followed.

3.49.7 Inspection and Monitoring

- a) Oxygenated water corrosion is typically localized, so inspection plans and practices need to take this into account. The focus should be on high-velocity and turbulent areas and stagnant or low-flow areas.
 1. Both straight run piping and fittings can be affected. The full circumference of piping and components should be inspected.
 2. Specific areas to check include downstream of ejectors, control valves, throttled valves, pumps, flow orifices, and internal protrusions, as well as at elbows, tees, and reducers.

3. Check the top of piping where condensing conditions exist.
 4. Check the bottom of piping and small-bore connections where a separate water phase or cooler conditions exist.
 5. Check the water/vapor interface, if one exists.
- b) RT, manual UT scanning or grid UT, and AUT are suitable NDE methods.
 - c) Permanently mounted thickness monitoring sensors can be used.
 - d) O₂ content less than 100 ppb in non-aerated water systems is very difficult to measure, so consult a specialist, as needed, to ensure the correct procedures for sampling and monitoring the water are used.

3.49.8 Related Mechanisms

Cooling water corrosion (3.20), boiler water and condensate corrosion (3.9), brine corrosion (3.10), and concentration cell corrosion (3.19).

3.49.9 References

1. *ASM Metals Handbook*, ASM International, Materials Park, OH, 1985, p. 4.91.
2. M.G. Fontana, *Corrosion Engineering*, Third Edition, 1987, p. 17.
3. K.L. Heidersbach, "Hungry Water Corrosion Testing," Chevron Corp. Energy Technology Company, 2011.
4. N. Fredj, T.D Burleigh, K L. Heidersbach, and B.R. Crowder, "Corrosion of Carbon Steel in Waters of Varying Purity and Velocity," Paper No. 1461, *Corrosion/2012*, NACE International, Houston, TX.

3.50 Phenol (Carbolic Acid) Corrosion

3.50.1 Description of Damage

Corrosion of carbon steel can occur in plants using phenol as a solvent to remove aromatic compounds from lubricating oil feedstocks.

3.50.2 Affected Materials

In order of increasing resistance: carbon steel, 304L, 316L, and Alloy C276.

3.50.3 Critical Factors

- a) Temperature, water content, alloy chemistry, and flow velocity are the critical factors.
- b) The corrosion rate of carbon steel at temperatures less than 212 °F (100 °C) is typically 1 mpy to 2 mpy.
- c) The corrosion rate of carbon steel exceeds 20 mpy above 350 °F (175 °C).
- d) Carbon steel and 304/304L stainless steel corrode rapidly in phenol service above 500 °F (260 °C).
- e) Dilute aqueous solutions (5 % to 15 % phenol) can be very corrosive.
- f) High velocities may promote localized corrosion (i.e. erosion-corrosion), particularly at velocities greater than 30 ft/s.

3.50.4 Affected Units or Equipment

- a) Phenol extraction facilities in lube oil plants.
 - 1. Corrosion is usually minimal in the treating section when the temperature is below 250 °F (121 °C).
 - 2. Corrosion can occur in the recovery section where spent phenol is separated by vaporization.
 - 3. Sulfur and organic acids may lead to naphthenic acid attack and sulfidation in the hot extract circuit.
 - 4. Dilute aqueous solutions (5 % to 15 % phenol) are very corrosive to the extract dryer condensers.
 - 5. Erosion-corrosion and/or condensation corrosion may be observed in tower overhead circuits.

3.50.5 Appearance or Morphology of Damage

- a) Corrosion will be general or localized, with local corrosion often being the result of erosion-corrosion.

3.50.6 Prevention/Mitigation

- a) Corrosion is best prevented through proper materials selection and control of phenol solvent chemistry.
- b) Velocity in carbon steel should be limited to less than 30 ft/s
- c) Overhead piping circuits should be designed for a maximum velocity of 30 fps in the recovery section.
- d) Recovery tower overhead temperatures should be maintained to at least 30 °F (15 °C) above the dew point.
- e) Type 316L stainless steel may be effective in the top of the dryer tower, phenol flash tower, and various condenser shells and separator drums that handle phenol-containing water.
- f) Tubes and headers in extract furnaces should be 316L.

- g) Alloy C276 has been used in areas of high velocity or other locations where 316L is inadequate.

3.50.7 Inspection and Monitoring

- a) VT can be used for accessible internal surfaces at liquid impingement and turbulent flow areas and is often followed up with UT thickness measurements in suspect areas.
- b) External UT can be used to identify, map, and monitor loss in thickness.
- c) RT, where practical considering pipe diameter, can be effective for identifying localized attack.
- d) Permanently mounted thickness monitoring sensors can be used.
- e) ER corrosion probes and corrosion coupons have been used for corrosion monitoring.

3.50.8 Related Mechanisms

Erosion/erosion-corrosion ([3.27](#)).

3.50.9 References

1. J. Gutzeit, R.D. Merrick, and L.R. Scharfstein, "Corrosion in Petroleum Refining and Petrochemical Operations," *Metals Handbook*, Volume 13, ASM International, Materials Park, OH, 1987, pp. 1262–1287.

3.51 Phosphoric Acid Corrosion

3.51.1 Description of Damage

Phosphoric acid is most often used as a catalyst in polymerization units. It can cause corrosion of carbon steel, depending on water content. Corrosion is typically localized to where the conditions for causing corrosion exist.

3.51.2 Affected Materials

For materials typically used or considered for this application, the order of increasing resistance is carbon steel, 304L SS, 316L SS, Alloy 20, and Alloy 825. The "L" (low carbon content) grades of stainless steels are preferable to straight grades to reduce the risk of sensitization and intergranular corrosion.

3.51.3 Critical Factors

- a) Acid concentration, water content (i.e. the presence of water), temperature, and contaminants are the critical factors.
- b) Solid phosphoric acid catalysts are not corrosive to carbon steel unless free water is present. When water is present, severe corrosion of carbon steel may occur.
 - 1. A small amount of water in contact with the catalyst can create a very concentrated (non-diluted) acid.
 - 2. Corrosion can penetrate a ¼-in. (6-mm) thick steel tube in 8 hr.
- c) Corrosion rates increase with increasing temperature.
- d) Contaminants such as chlorides, fluorides, and other halide salts can increase phosphoric acid corrosion rates.
- e) Most corrosion probably results from water washing operations during shutdowns.
- f) Low points that may collect water are subject to localized corrosion.

3.51.4 Affected Units or Equipment

- a) Piping and equipment in polymerization units where water mixes with catalyst.
- b) Corrosion is usually found in low points and low-velocity areas where there is little or no circulation. Examples include piping manifolds, bypass lines, dead-legs, partial penetration welds, the bottom of kettle-type reboilers, and exchangers where there is sufficient residence time to permit the settling of acid droplets.

3.51.5 Appearance or Morphology of Damage

The corrosion mainly occurs as localized thinning with either a pitted or more general (smoother) appearance on the attacked carbon steel surface. Sensitized stainless steel will suffer intergranular corrosion.

3.51.6 Prevention/Mitigation

- a) Water content (i.e. moisture content) should be limited to less than 400 ppm.
- b) Where water cannot be eliminated, selective upgrading to corrosion-resistant materials is the practical option.
- c) Type 304L SS is satisfactory for phosphoric acid concentration of 100 % up to about 120 °F (50 °C). Type 316L SS is required from 120 °F to 225 °F (50 °C to 105 °C).
- d) Type 316L SS and Alloy 20 are effective at concentrations up to 85 % at boiling temperatures.

- e) At even higher temperatures above boiling, where the liquid acid is still present, Alloy 825 may be needed.

3.51.7 Inspection and Monitoring

- a) UT and RT can be used to detect and measure loss of thickness.
- b) Permanently mounted thickness monitoring sensors can be used.
- c) The water from the first column overhead receiver should be monitored for iron content. In addition, it is advisable to monitor temperatures, pH, water content (e.g. by installing a moisture analyzer), and for phosphoric acid carryover past the reactor.
- d) Online corrosion monitoring can be performed using ER probes and/or corrosion coupons in the water draw from the first column overhead condenser and the reboiler.

3.51.8 Related Mechanisms

Although corrosion is caused by a number of strong and weak acids in the refining industry, phosphoric acid corrosion is specific to polymerization units. Where caustic neutralization is employed in polymerization units, if the resulting salts are not properly separated out, wet, corrosive solids may deposit and cause under-deposit corrosion. (See [3.19](#).)

3.51.9 References

1. R.A. White and E.F. Ehmke, *Materials Selection for Refineries and Associated Facilities*, NACE International, Houston, TX.
2. *Corrosion Control in the Refining Industry*, NACE Course Book, NACE International, Houston, TX, 1999.

3.52 Polythionic Acid Stress Corrosion Cracking

3.52.1 Description of Damage

- a) Intergranular SCC that can occur in sensitized austenitic stainless steels and some Ni alloys (Alloy 800 and Alloy 600) when sulfide scale formed on the surface during operation is exposed to air and moisture. The combination of sulfide scale, air (i.e. oxygen), and moisture creates sulfur acids on the surface that then cause polythionic acid stress corrosion cracking (PTA SCC). It normally occurs during shutdowns or start-ups.
- b) Usually occurs adjacent to welds or in high-stress areas.
- c) Cracking may propagate rapidly through the wall thickness of piping and components in a matter of minutes or hours.

3.52.2 Affected Materials

Austenitic stainless steels (300 series SS) and austenitic alloys (Alloy 600/600H and Alloy 800/800H/800HT). Alloys 625 and 825 are also susceptible but require extended periods at much higher temperatures [$>1200^{\circ}\text{F}$ (650°C)] to sensitize.

3.52.3 Critical Factors

- a) A combination of environment, susceptible material, and tensile stress are required.
 - 1. Environment—Susceptible metals form a surface sulfide scale when exposed to sulfur compounds in a high-temperature reducing process environment. The scale may then react with air (oxygen) and moisture to form sulfur acids (polythionic acids, $\text{H}_2\text{S}_x\text{O}_6$).
 - 2. Material—The material must be susceptible to sensitization and in a sensitized condition.
 - 3. Tensile Stress—The stress can be residual or applied.
- b) Affected alloys become sensitized during exposure to elevated temperatures during manufacture, welding, or high-temperature service. Sensitization refers to the composition/time/temperature-dependent formation of chromium carbides in the grain boundaries of the metal. Sensitization occurs in the 700°F to 1500°F (370°C to 815°C) temperature range. However, chemically stabilized grades of stainless steel, e.g. Types 321 and 347, can withstand service temperatures greater than 700°F without suffering detrimental sensitization. Some refiners permit the use of these alloys at temperatures substantially greater than 700°F without requiring thermal stabilization.
- c) The carbon content and the thermal history of the alloy have a significant effect on sensitization susceptibility. Regular and high carbon grades of stainless steels such as Types 304/304H and 316/316H are particularly susceptible to sensitizing in the weld HAZ. Low carbon “L” grades ($<0.03\%$ C) are less susceptible and usually can be welded without sensitizing. The L grades will not sensitize provided long-term operating temperatures do not exceed about 750°F (400°C).
- d) Residual tensile stresses in most components, especially in non-stress-relieved welds, are usually sufficient to promote cracking and are the most common source of the tensile stress needed to cause cracking.

3.52.4 Affected Units or Equipment

- a) All units where sensitized alloys are used in high-temperature sulfur-containing environments. Commonly damaged equipment includes heat exchanger tubes and components, furnace tubes, and piping.
- b) Fired heaters burning oil, gas, coke, and most other sources of fuel may be affected depending on sulfur levels in the fuel and combustion conditions in the firebox. (Fuel-rich conditions will favor formation of sulfide scales instead of oxide scales.) In places where there are environmental restrictions on the burning of high sulfur fuels, the occurrences of fire-side PASCC have diminished.

- c) FCC Units—Air rings, plenums, slide valves, cyclone components, expansion joint bellows, and piping.
- d) Hydroprocessing Units—Heater tubes, hot feed/effluent exchanger tubes, pressure vessels (including heat exchangers and reactors), piping, and bellows.
- e) Crude and Coker Units—Heater tubes and piping.
- f) Boilers and other high-temperature equipment exposed to sulfur-containing combustion products can also be susceptible if sensitized alloys are involved.

3.52.5 Appearance or Morphology of Damage

- a) Typically occurs next to welds (Figure 3-52-1 and Figure 3-52-4) but can also occur in the base metal. It is usually quite localized and may not be evident until a leak appears during start-up or, in some cases, operation.
- b) Cracking propagates intergranularly. (Figure 3-52-2 and Figure 3-52-5)
- c) Corrosion or loss in thickness is usually negligible.

3.52.6 Prevention/Mitigation

- a) If potentially susceptible equipment will be opened or exposed to air, preventive measures should be taken to minimize or eliminate PTA SCC. These include (i) flushing the equipment during or immediately after shutdown with alkaline or soda ash solution to neutralize the acids formed after shutdown and exposure to air and moisture or (ii) purging with dry nitrogen or nitrogen/ammonia during the shutdown to prevent air exposure and the formation of polythionic acids. Refer to guidelines in NACE SP0170.
- b) Furnace tubes that have coke on the tube ID should undergo some form of decoking process prior to or concurrent with the alkaline washing if the tube IDs will be exposed to air. Alkaline washing with coke present has low effectiveness. Refer to NACE SP0170 for guidance.
- c) Keeping the firebox heated above the dew point to prevent acids from forming on the heater tube internal surfaces, if practical, will also prevent PTA SCC. This can also be accomplished by using dehumidification equipment to reduce the water dew point inside the tubes below ambient.
- d) Low carbon grades of stainless steel such as 304L, 316L, and 317L provide some measure of improvement over higher carbon grades. The L grades will sensitize if exposed more than several hours above about 1000 °F (540 °C) or long-term above 750 °F (400 °C).
- e) Improved resistance to PTA SCC cracking can be achieved with chemically stabilized versions of these alloys containing small amounts of titanium (Ti) or niobium (Nb) and tantalum (Ta). [Note that niobium was also called columbium (Cb), but niobium is now the generally accepted name.] Types 321 and 347 SS are the chemically stabilized grades of austenitic stainless steel most commonly used. Alloy 20Cb-3 as well as Alloys 825 and 625 are also chemically stabilized.
- f) Supplemental requirements in ASTM specifications provide for mill products to be delivered in a thermally stabilized condition rather than simply solution annealed. This heat treatment will minimize potential sensitization problems at higher temperatures, e.g. as found in a heater.
- g) A thermal stabilization heat treatment at 1650 °F (900 °C) may be applied to chemically stabilized austenitic stainless steel welds after all welding is complete to reduce sensitization and PTA SCC susceptibility at the welds. This heat treatment is also applied after welding material that was thermally stabilized in the mill in order to restore the thermal stabilization destroyed by the heat of welding.
- h) The degree of sensitization and resultant susceptibility to PTA SCC can be determined by laboratory corrosion testing according to ASTM A262 Practice C. This test is also used as a quality control check at the

mill on chemically stabilized grades, with a sensitizing heat treatment applied prior to testing in order to assess resistance to sensitization.

3.52.7 Inspection and Monitoring

- a) PTA SCC is most effectively managed by prevention rather than through inspection. PTA SCC can be an inspection challenge because the cracking may not occur until well into a turnaround.
- b) Monitoring for PTA SCC cracking during operation is not effective. Conditions causing the cracking are not usually present while the unit is online.
- c) PT examination is the most common method used to detect PTA SCC. (Figure 3-52-1 and Figure 3-52-3) However, because the cracks are filled with a tight deposit, flapper wheel sanding or grinding may be needed to improve the PT sensitivity.
- d) ECT can detect surface cracks on the crack initiation side.
- e) AET has had some success in detecting and locating PTA SCC. However, results sometimes can be inconclusive, and quality AET data may be difficult to obtain.
- f) Angle beam UT (SWUT and PAUT) crack detection techniques may be useful depending on thickness, metallurgy, and accessibility considerations and limitations.
- g) FMR can be used to determine the degree and extent of sensitization.

3.52.8 Related Mechanisms

Intergranular corrosion and intergranular attack.

3.52.9 References

1. *ASM Handbook—Corrosion*, Volume 13, ASM International, Materials Park, OH, p. 327.
2. NACE SP0170, *Protection of Austenitic Stainless Steels and Other Austenitic Alloys from Polythionic Acid Stress Corrosion Cracking During a Shutdown of Refinery Equipment*, NACE International, Houston, TX.
3. D.V. Beggs, and R.W. Howe, "Effects of Welding and Thermal Stabilization on the Sensitization and Polythionic Acid Stress Corrosion Cracking of Heat and Corrosion-resistant Alloys," Paper No. 541, *Corrosion/93*, NACE International, Houston, TX.
4. L. Scharfstein, "The Effect of Heat Treatments in the Prevention of Intergranular Corrosion Failures of AISI 321 Stainless Steel," *Materials Performance*, September 1983, pp. 22–24.
5. E. Lendvai-Linter, "Stainless Steel Weld Overlay Resistance to Polythionic Acid Attack," *Materials Performance*, Vol. 18, No. 3, 1979, p. 9.
6. J. E. Cantwell, "Embrittlement and Intergranular Stress Corrosion Cracking of Stainless Steels After Elevated Temperature Exposure in Refinery Process Units," *Proceedings of the API Division of Refining Midyear Meeting*, May 1984.
7. R.L. Piehl, "Stress Corrosion Cracking by Sulfur Acids," *Proceedings of the API Division of Refining*, Vol. 44, No. 3, 1964, pp. 189–197.
8. C.H. Samans, "Stress Corrosion Cracking Susceptibility of Stainless Steels and Nickel-base Alloys in Polythionic Acids and Acid Copper Sulfate Solution," *CORROSION*, Vol. 20, No. 8, NACE International, Houston TX, 1994, pp. 256–262.

9. C.D. Stevens and R.C. Scarberry, "The Relation of Sensitization to Polythionic Acid Cracking of Incoloy Alloys 800 and 801," *Proceedings of the 25th Conference*, NACE International, Houston, TX, 1969, pp. 583–586.
10. E. Nagashima, K. Matsumoto, and K. Shibata, "Effects of Sensitization and Service Fluid Chemistry on Polythionic Acid Stress Corrosion Cracking of 18-8 Stainless Steels," Paper No. 592, *Corrosion/98*, NACE International, Houston, TX.

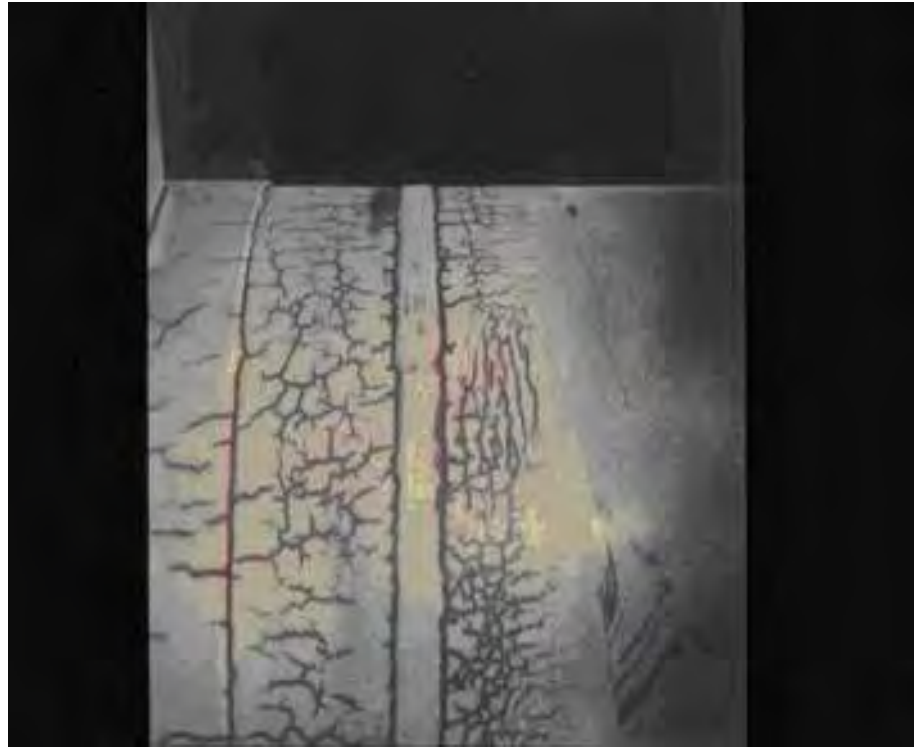


Figure 3-52-1—Dye penetrant (PT) inspection showing extensive OD PTA SCC around welds.

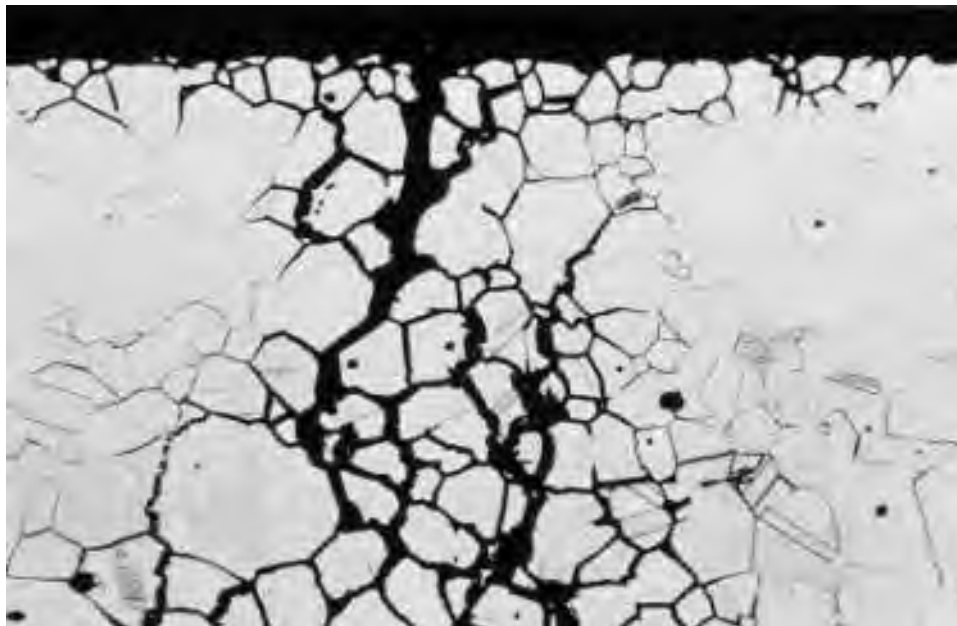


Figure 3-52-2—High-magnification photomicrograph of metallographic sample showing intergranular cracking and grain dropping.

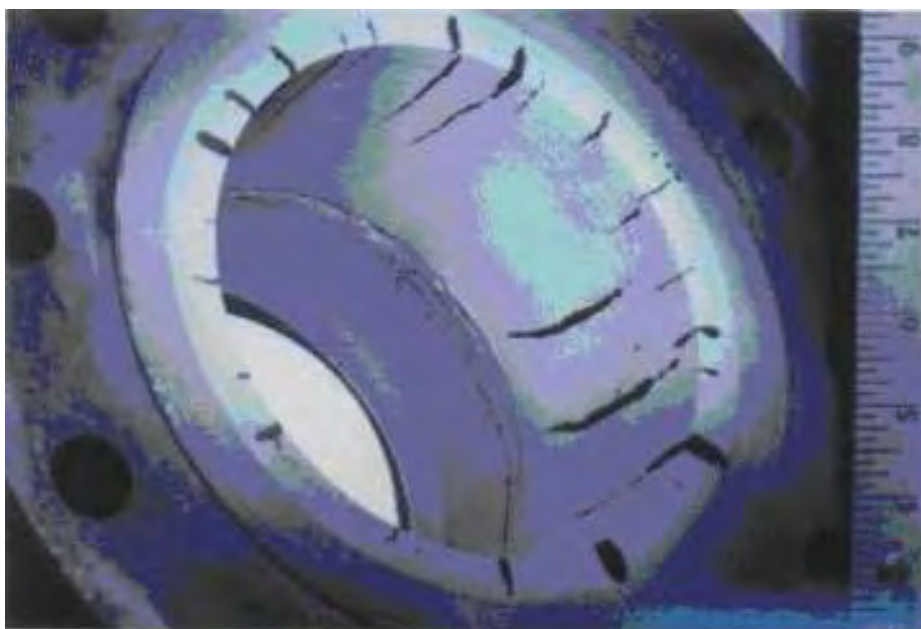


Figure 3-52-3—PT inspection of a Type 304 stainless steel catalyst withdrawal line piping and weld neck flange.



Figure 3-52-4—Cross section of the catalyst withdrawal line attached to the flange in Figure 3-50-3 showing cracking in the weld HAZ. Magnification 3X.

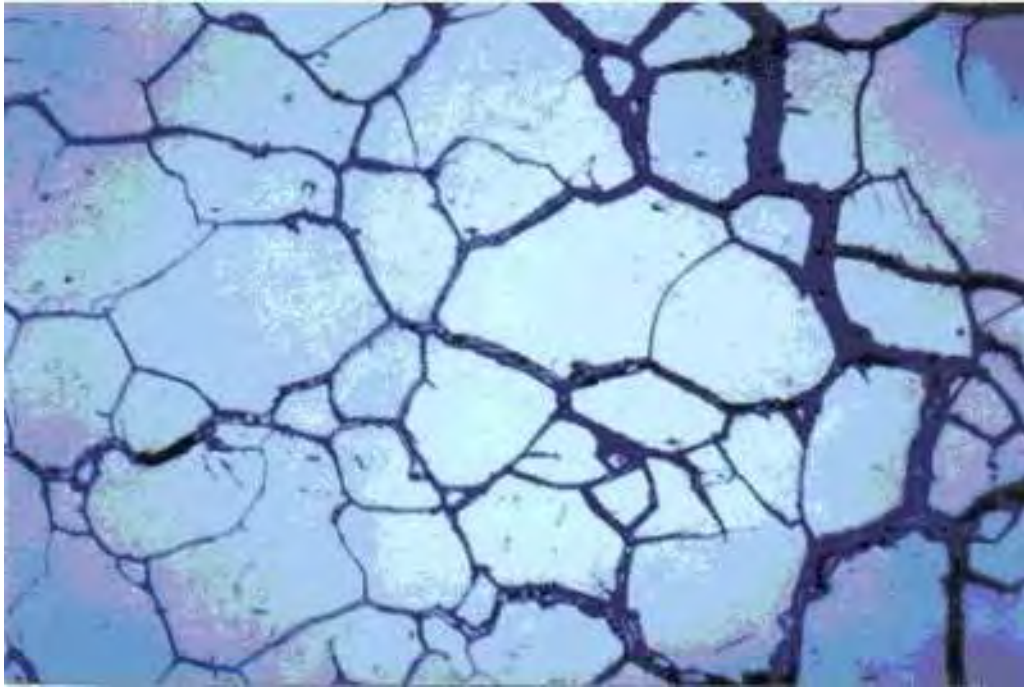


Figure 3-52-5—Higher-magnification view showing intergranular cracking. Magnification 200X.

3.53 Refractory Degradation

3.53.1 Description of Damage

Both thermally insulating and erosion-resistant refractories are susceptible to various forms of mechanical damage (cracking, spalling, and erosion) as well as corrosion due to oxidation, sulfidation, and other high-temperature mechanisms. High skin temperatures on the base metal being protected may result from refractory damage.

3.53.2 Affected Materials

Refractory materials include insulating ceramic fibers, castables, refractory brick, and plastic refractories.

3.53.3 Critical Factors

- a) Refractory design, selection, and installation are the keys to minimizing damage. Anchor materials need to be selected properly. Process environment factors are also critical.
- b) Refractory lined equipment should be designed to handle the erosion, thermal shock, and thermal expansion to be encountered in service.
- c) Refractory type and density need to be selected to resist abrasion and erosion based on service requirements.
- d) Needles and other fillers need be compatible with the process environment composition and temperature.
- e) Dryout schedules, cure times, and application procedures should be in accordance with the manufacturer's specifications and the appropriate ASTM requirements.
- f) Anchor materials need to be compatible with the thermal coefficient of expansion of the base metal.
- g) Anchors need to be resistant to oxidation in high-temperature services.
- h) Anchors need to be resistant to condensing sulfurous acids in heaters and flue gas environments.
- i) In erosive services, refractory may be washed away or thinned, exposing the anchoring system. ([Figure 3-53-1](#))
- j) Coke deposits may develop behind refractory and promote cracking and deterioration.
- k) Refractories can suffer vibration damage.
- l) Refractories can be damaged by exposure to moisture.

3.53.4 Affected Units or Equipment

- a) Refractories are extensively used in FCC reactor regenerator vessels, piping, cyclones, slide valves, and internals.
- b) Refractories are also used in fluid coker units, in cold shell catalytic reforming reactors, and in waste heat boilers and thermal reactors in sulfur plants.
- c) Boiler and heater fireboxes, floors, and stacks that use refractory are also affected.

3.53.5 Appearance or Morphology of Damage

- a) Refractory may show signs of excessive cracking, spalling or lift-off from the substrate, softening, or general degradation.

- b) A potential warning sign of vibration damage to refractories is visible damage and failure of the refractory or the anchoring system.

3.53.6 Prevention/Mitigation

- a) Proper selection, design, and installation of refractory, anchors, and fillers are the keys to minimizing refractory damage and failure.
- b) Operating parameters should be monitored to identify process upsets (e.g. temperature excursions or loss of flame) and cyclic operation that may impact the integrity and effectiveness of the refractory lining. Refractory degradation should be taken into account as a potential damage mechanism when selecting IOWs.

3.53.7 Inspection and Monitoring

- a) Refractory and ferrules (tubesheets) should be visually inspected looking for signs of chemical degradation or mechanical degradation (e.g. spalling, slumping, or cracking of ferrules) during equipment outages.
- b) For FCC vessels, hammer testing can be used in areas known for channeling behind the refractory.
- c) Cold-wall equipment can be surveyed while onstream using IR thermography, or at least VT where temperature indicating paint has been applied or where paint is badly discolored or burnt, to monitor for hot spots and help identify potential refractory damage.

3.53.8 Related Mechanisms

Oxidation (3.48), sulfidation (3.61), flue gas dew point corrosion (3.29), HTHA (3.36), decarburization (3.25), carburization (3.13), and metal dusting (3.44).

3.53.9 References

1. R.A. White and E.F. Ehmke, *Materials Selection for Refineries and Associated Facilities*, NACE International, Houston, TX, 1991, pp. 33, 57.



Figure 3-53-1—Damaged refractory and ferrules.

3.54 Stress Relaxation Cracking (Reheat Cracking)

3.54.1 Description of Damage

Cracking of a metal due to stress relaxation via grain boundary strain in the creep temperature range during PWHT or in service at elevated temperatures. The temperature above which it occurs depends on the type of alloy. It is most often observed in heavy wall sections. At various times and in various situations, stress relaxation cracking (SRC) has also been called reheat cracking, stress-relief cracking, creep embrittlement, low creep ductility cracking, stress-induced cracking, and stress-assisted grain boundary oxidation cracking.

3.54.2 Affected Materials

- a) Cr-Mo steels, especially 2¼Cr-1Mo steel with vanadium added, 1Cr-½Mo, and 1¼Cr-½Mo.
- b) Types 304H, 316H, 321, and 347 SS.
- c) Nickel-based alloys, particularly Alloy 800H, 800HT, Alloy 617, and centrifugally cast 22Cr-35Ni-Nb used for heavy wall piping and headers in hydrogen reformer heaters.
- d) HSLA steels are very susceptible.

3.54.3 Critical Factors

- a) In addition to exposure to elevated temperature in the creep range, important parameters include the type of material (chemical composition, impurity elements), grain size, weld metal and base metal strength, residual stresses from fabrication (cold working, welding), section thickness (which controls restraint and stress state), notches and stress concentrators, and welding and heat treating applied.
- b) SRC occurs at elevated temperatures when creep ductility is insufficient to accommodate the strains required for the relief of applied or residual stresses.
 - 1. The affected alloys contain alloying additions that promote fine intragranular precipitate particles that make the grains stronger than the grain boundaries and force the creep deformation to be concentrated at the grain boundaries.
 - 2. Impurity elements like phosphorous, tin, antimony, and arsenic, if present, also promote SRC, particularly in Cr-Mo low-alloy steels, because they concentrate at grain boundaries and limit grain boundary ductility.
- c) SRC can either occur during PWHT or in service at high temperature. In both cases, cracks are intergranular and show little or no evidence of deformation.
- d) The approximate temperatures above which, or ranges within which, SRC occurs for different types of alloys are as follows:
 - 1. 2¼Cr-1Mo-V: 840 °F (450 °C);
 - 2. 1Cr-½Mo and 1¼Cr-½Mo: 900 °F (480 °C);
 - 3. Types 347, 321, and 304H SS: 930 °F (500 °C) to 1380 °F (750 °C); and
 - 4. nickel-based alloys: 930 °F (500 °C) to 1380 °F (750 °C)
- e) SRC is normally more prevalent where large grain size exists, particularly in the low-alloy steels, e.g. in the coarse-grained HAZ. Large grain size means less total grain boundary volume to accommodate the creep strain, i.e. the creep strain is concentrated in a relatively small grain boundary volume.

- f) SRC requires the presence of high stresses and is therefore more likely to occur in thicker sections and higher-strength materials, including higher strength resulting from original plate mill heat treatments as in the case of 1Cr-½Mo and 1¼Cr-½Mo steel grades.
- g) Stress relief and stabilization heat treatment of Types 321 and 347 SS for maximizing Cl⁻ SCC and/or PASCC resistance can cause SRC problems, particularly in thicker sections.
- h) In the first half of 2008, numerous cases of SRC, primarily referred to as reheat cracking, occurred during 2¼Cr-1Mo-V reactor fabrication. The cracks were in weld metal only, transverse to the welding direction, and in only submerged-arc welding (SAW) welds. It was traced to a contaminant in the welding flux. A weld material screening test has since been implemented, as described in API 934-A.

3.54.4 Affected Units or Equipment

- a) Catalytic reformer and FCC units.
 - 1. Hot-wall 1Cr-½Mo and 1¼Cr-½Mo vessels and piping operated above 900 °F (480 °C), especially at the toe of nozzle-to-shell welds and reinforcement pads or wherever there is high restraint or high stress concentrations, including high pipe loads on pipe circumferential welds. "Peaking" greater than 1/16 in. (1.6 mm) in the longitudinal weld seams of welded pipe also increases the likelihood of SRC.
 - 2. This cracking has also been referred to as low creep ductility cracking and creep embrittlement cracking.
- b) Hydroprocessing.
 - 1. SRC can occur in heavy wall Type 321 and 347 SS effluent piping during fabrication PWHT, e.g. postweld stabilization heat treatment, or when welding is performed after being in service.
 - 2. Type 321 and 347 SS outlet piping from the recycle hydrogen heater to the reactor inlet line can operate hot enough to be susceptible to SRC during operation.
 - 3. Cracking can occur in Cr-Mo heavy wall reactor vessels during fabrication.
- c) Hydrogen manufacturing units.
 - 1. SRC has occurred in stainless steel tubes and piping in units that have a preconverter and a feed preheat coil.
 - 2. SRC has occurred in stainless steel and Alloy 800H steam superheater tubes.
- d) High-pressure steam piping.
 - 1. 1Cr-½Mo and 1¼Cr-½Mo piping operating above 900 °F (480 °C) with circumferential welds having significant stress risers and high applied loads.

3.54.5 Appearance or Morphology of Damage

- a) SRC is intergranular and can be surface breaking or embedded depending on the state of stress and geometry. It is most frequently observed in coarse-grained sections of a weld HAZ; however, it can also occur in weld deposits. ([Figure 3-54-1](#) to [Figure 3-54-4](#))
- b) In many cases, cracks initiate at some type of stress concentration. Once initiated, SRC cracks can enable further propagation by fatigue cracking.

3.54.6 Prevention/Mitigation

- a) Joints and nozzles in 1Cr-½Mo and 1¼Cr-½Mo vessels and piping, especially heavy wall sections, should be designed to minimize stress concentration as well as restraint during welding and PWHT. Adequate preheat must also be applied.
- b) In design and fabrication, it is advisable to avoid sharp changes in cross section, such as short radius fillets or undercuts that can give rise to stress concentrations. Long-seam welds are particularly susceptible to mismatch caused by fit-up problems or by “peaking” due to the plate edges not being properly rolled.
- c) Metallurgical notches arising from the welding operation are frequently the cause of cracking at the boundary between the weld and the HAZ.
- d) For 1Cr-½Mo and 1¼Cr-½Mo vessels operating above 900 °F (480 °C), follow the material grade and PWHT temperature guidelines in API 934-E.
- e) For 2¼Cr-1Mo-V welds, consider the recommendations for welding material screening tests in API 934-A.
- f) For thick-wall Type 321 or 347 SS piping, consider the possibility of SRC in deciding whether to PWHT. Also, minimize constraint, pipe loads, and stress concentrations at welds.
- g) For Alloy 800H, the risk of in-service cracking can be reduced by using base metal and matching weld metal with Al+Ti < 0.7 %.
- h) For Alloy 800H and 800HT, which will operate at >1000 °F (540 °C), the material may need to be purchased with a thermal stabilization heat treatment and with PWHT of welds and cold-worked sections. Welds should be made with matching Alloy 800H or 800HT filler material and should be stress relieved. Refer to UNF-56(e) in ASME BPVC Section VIII, Division 1 and to API 942-B for additional information.
- i) Low heat input welding procedures help minimize grain coarsening in the HAZ.
- j) Heating rates at temperatures above 480 °F (250 °C) should generally comply with the limits provided by ASME BPVC Section VIII for PWHT.

3.54.7 Inspection and Monitoring

- a) For Cr-Mo steels, surface cracks can be detected with WFMT, MT, or PT.
- b) For Type 321 and 347 SS as well as the nickel-based alloys, PT or angle beam UT (SWUT or PAUT) examination can be used to detect cracks.
- c) Special procedures, equipment, and interpretation are often required for angle beam UT inspection of austenitic materials with a thickness greater than ¾ in. (19 mm) compared to similar thickness non-austenitic materials.
- d) Embedded cracks can only be found by UT examination.
- e) Inspection for cracking in 2¼Cr-1Mo-V reactors during fabrication is typically done with TOFD and/or angle beam UT (SWUT or PAUT), with the demonstration block having defects as small as 3-mm side-drilled holes, as described in API 934-A.

3.54.8 Related Mechanisms

Creep and stress rupture (3.23). SRC has also been referred to as reheat cracking, stress-relief cracking, creep embrittlement, low creep ductility cracking, stress-induced cracking, and stress-assisted grain boundary oxidation cracking.

3.54.9 References

1. R. Viswanathan, *Damage Mechanisms and Life Assessment of High-temperature Components*, ASM International, Materials Park, OH.
2. D.N. French, *Metallurgical Failures in Fossil Fired Boilers*, Second Edition, John Wiley and Sons, New York, NY, 1993, pp. 455–458.
3. A. Dhooge, “Survey on Reheat Cracking in Austenitic Stainless Steels and Ni Base Alloys,” IIW-Commission IX, Doc. IX-1876–97.
4. C.D. Lundin and D.K.K. Khan, *Fundamental Studies of the Metallurgical Causes and Mitigation of Reheat Cracking in 1¼Cr-½Mo and 2¼Cr-1Mo Steels*, WRC Bulletin 409, Welding Research Council, Shaker Heights, OH.
5. C. Shargay and A. Singh, “Thick Wall Stainless Steel Piping in Hydroprocessing Units—Heat Treatment Issues,” Paper No. 02478, *Corrosion/2002*, NACE International, Houston, TX.
6. M.E. Fahrion et al., “Technical Basis for Improved Reliability of 347H Stainless Steel Heavy Wall Piping in Hydrogen Service,” Paper No. 03647, *Corrosion/2003*, NACE International, Houston, TX.
7. T. Kiso, K. Ishii, and I. Seshimo, “Cracking in Welds of Heavy-wall Stainless Steel and Nickel Alloy Piping During Fabrication,” Paper PVP2009-77554, *ASME PVP Conference*, New York, NY, 2009.
8. J.J. Hoffman and G.Y. Lai, “Metallurgical Evaluation of Alloy 800HT Pigtails,” Paper No. 05402, *Corrosion/2005*, NACE International, Houston, TX.
9. H. Van Wortel, “Control of Relaxation Cracking in Austenitic High Temperature Components,” Paper No. 07423, *Corrosion/2007*, NACE International, Houston, TX.
10. C.E. van der Westhuizen, “Stress Relaxation Cracking of Welded Joints in Thick Sections of a TP347 Stabilized Grade of Stainless Steel,” Paper No. 08454, *Corrosion/2008*, NACE International, Houston, TX.
11. API Technical Report 942-B, *Material, Fabrication, and Repair Considerations for Austenitic Alloys Subject to Embrittlement and Cracking in High Temperature 565 °C to 760 °C (1050 °F to 1400 °F) Refinery Services*, American Petroleum Institute, Washington, DC, May 2017.
12. API Recommended Practice 934-A, *Materials and Fabrication of 2¼Cr-1Mo, 2¼Cr-1Mo-¼V, 3Cr-1Mo, and 3Cr-1Mo-¼V Steel Heavy Wall Pressure Vessels for High-temperature, High-pressure Hydrogen Service*, American Petroleum Institute, Washington, DC.
13. API Recommended Practice 934-E, *Recommended Practice for Materials and Fabrication of 1¼Cr-½Mo Steel Pressure Vessels for Service Above 825 °F (440 °C)*, American Petroleum Institute, Washington, DC.
14. M.S. Cayard and M.S. Geisenhoff, “Detriment of Peaking on Longitudinal Welds in CCR Heater Transfer Lines and Methods for Inspection,” Paper 140, *API Inspection Summit 2017*, January 2017.
15. P.E. Prueter, J.D. Dobis, M.S. Geisenhoff, and M.S. Cayard, “Remaining Life Sensitivity to Longitudinal Weld Seam Peaking in High-temperature Low Chrome Piping,” *Inspectioneering Journal*, Vol. 22, Issue 4, July/August 2016.
16. P.E. Prueter, J.D. Dobis, M.S. Geisenhoff and M.S. Cayard, “A Computational Study of the Creep Response of High-Temperature Low Chrome Piping with Peaked Longitudinal Weld Seams,” Paper PVP2016-63582, *ASME Pressure Vessels and Piping Division Conference*, 2016.
17. A. Cheta, R. Konet, and F. Hoyt, “Fitness for Service and Remaining Life Assessment for 1¼Cr-½Mo Reactor System Piping on a Catalytic Reformer Unit,” Paper PVP2006-ICPVT-93275, *ASME Pressure Vessels and Piping Division Conference*, 2006.



Figure 3-54-1—Samples removed from a cracked 12-in. NPS Type 321 SS elbow in a hot recycle H₂ line that operated at 985 °F (530 °C) in a hydrocracker.



Figure 3-54-2—Crack at weld from Type 321 SS elbow shown in Figure 3-52-1.

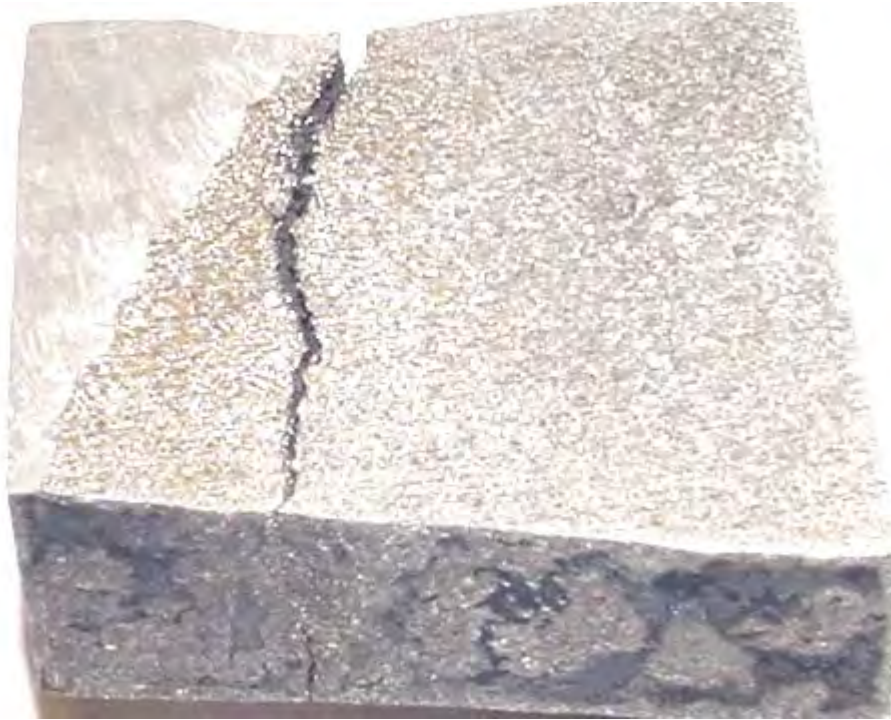


Figure 3-54-3—Cross section through the weldment showing the crack in Figure 3-52-2.

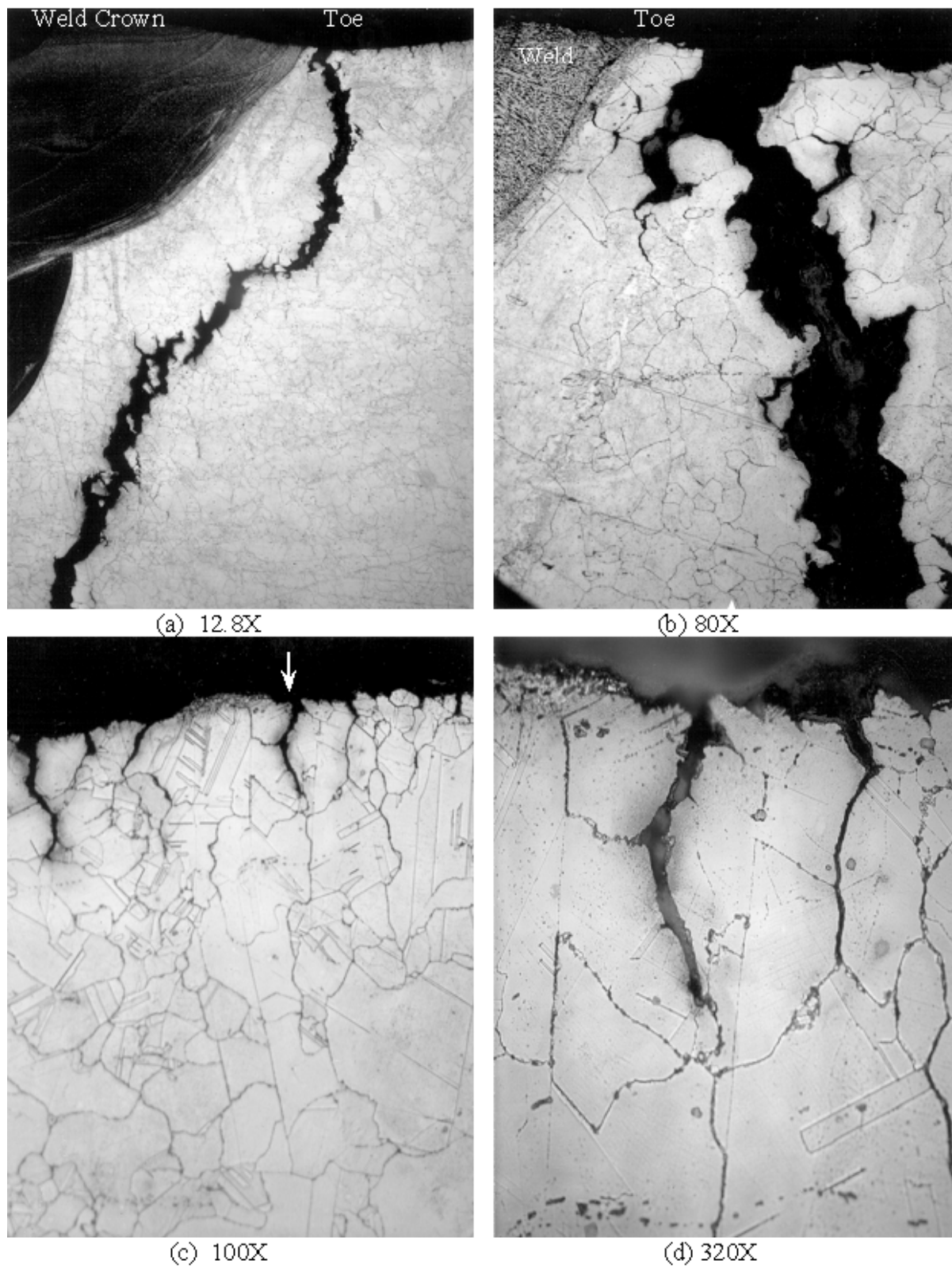


Figure 3-54-4—Photomicrographs of the weldment area shown in Figure 3-52-3.

3.55 Short-term Overheating—Stress Rupture (Including Steam Blanketing)

3.55.1 Description of Damage

Permanent deformation occurring at very high temperatures and typically relatively low stress levels as a result of localized overheating. It typically will result in bulging and eventual failure by stress rupture. If the temperature is high enough, failure will occur very quickly by tensile overload, since tensile strengths drop off dramatically at very high temperatures. At less severe temperatures, short-term creep failure will occur.

3.55.2 Affected Materials

All fired heater tube and boiler tube materials and common materials of construction.

3.55.3 Critical Factors

- a) Temperature, time, and stress are the critical factors.
- b) In heaters, it is usually due to flame impingement or any other cause of local overheating.
- c) In boiler tubes, it is due to steam blanketing (DNB), which may result from flame impingement or restricted water flow.
- d) The higher the internal pressure or loading, the shorter will be the time to failure. However, bulging and distortion can be significant even at low pressures and stresses if the temperature is high enough.
- e) The local overheating is well above the design temperature.
- f) Previous loss in thickness due to corrosion will reduce time to failure due to the increased stress on the remaining thickness.

3.55.4 Affected Units or Equipment

- a) All fired heater tubes are susceptible.
- b) Heaters with coking tendencies such as in crude, vacuum, heavy oil hydroprocessing, and coker units are often fired harder to maintain heater outlet temperatures and are thereby more susceptible to localized tube overheating. Flame impingement can also lead to localized overheating.
 - 1. Steam-air decoking can also create localized hot spots internally if the coke is burned out too aggressively.
- c) All steam-generating units including fired boilers and waste heat exchangers (steam generators) in process plants including sulfur plants, catalytic reformers, hydrogen reformers, and FCC units. Failures can occur in superheaters and reheaters during start-up when condensate blocks steam flow.
- d) Hydroprocessing reactors may be susceptible to localized overheating of reactor beds due to inadequate hydrogen quench or flow maldistribution.
- e) Catalytic reforming reactors may be susceptible to localized overheating due to coking of the catalyst.
- f) Refractory lined equipment in an FCC unit, sulfur plant, H₂ manufacturing plant, and other units may suffer localized overheating due to refractory damage and/or excessive firing.
- g) Heater fireboxes can suffer localized overheating due to loss of protective refractory or insulation.

3.55.5 Appearance or Morphology of Damage

- a) Damage is typically characterized by localized deformation or bulging on the order of 3 % to 10 % or more, depending on the alloy, temperature, and stress level.

- b) Tube ruptures are characterized by open “fishmouth” failure and are usually accompanied by a thin, knife-edged fracture surface resulting from the excessive deformation and bulging prior to failure. (Figure 3-55-1 to Figure 3-55-5)
- c) The microstructure of ruptured tubes will show severe elongation of the grains at the fracture surface due to the plastic deformation that occurs. (Figure 3-55-4)

3.55.6 Prevention/Mitigation

- a) Damage can be avoided by minimizing temperature excursions.
- b) Proper burner maintenance, management, and fouling/deposit control are needed to minimize hot spots and localized overheating in fired heaters and boilers.
- c) Burners that produce a more diffuse flame pattern should be used in heaters.
- d) Proper BFW treatment can help prevent some conditions that can lead to restricted flow in boilers.
- e) In hydroprocessing equipment, installing and maintaining bed thermocouples in reactors will help minimize the likelihood of hot spots. Proper system design and operation are also important.
- f) Refractory in refractory lined equipment should be maintained in serviceable condition.

3.55.7 Inspection and Monitoring

- a) Short-term overheating damage or failure can occur in such a short time that inspection as a mitigative or preventive measure may not be possible. However, there are several inspection and monitoring methods applicable to dealing with short-term overheating.
- b) Components that are accessible during shutdowns, particularly in fired heaters and boilers, can be visually inspected to find tube bulging, sagging, and other types of deformation. Damage can be quantified by strapping the tubing and taking UT thickness measurements. However, not all components can be checked. Inspection is limited to that which is within line-of-sight, and not all damage is visually apparent.
- c) Infrared thermography monitoring of heater tubes for localized hot spots could indicate locations susceptible to short-term overheating failures. This inspection is also limited to line-of-sight locations, but the technique can be employed while the equipment is in operation using either installed or portable IR thermography monitoring tools.
- d) Thermocouples can be installed to monitor temperatures of heater tubes as well as other equipment, including refractory lined equipment, during operation. Thermocouples can be attached directly to the metal surface or placed under insulation for approximate temperature measurement. However, thermocouples often cannot identify localized hot spots, because placement of thermocouples often does not coincide with the location of localized hot spots arising later.
- e) Refractory damage should be inspected during shutdowns as it may indicate possible short-term overheat damage or may provide clues for where to look for possible tube or other component overheat damage.
- f) FMR of accessible components can reveal the microstructure and is used to evaluate creep void formation. With knowledge of operating conditions, FMR may be employed for remaining life assessments of affected components.
- g) Steam blanketing that results in long-term localized caustic corrosion (3.14) rather than a short-term overheating failure may be detected by VT of the tube internals using a boroscope.
 - 1. Other localized thinning inspection techniques such as straight beam UT, PAUT, or TOFD can be used, but in the case where the steam generation tubes are finned, these techniques are not applicable.

3.55.8 Related Mechanisms

Creep/stress rupture (3.23) and caustic corrosion/caustic gouging (boilers) (3.14).

3.55.9 References

1. API 579-1/ASME FFS-1, *Fitness-For-Service*, American Petroleum Institute, Washington, DC.
2. API Standard 530, *Calculation of Heater-tube Thickness in Petroleum Refineries*, American Petroleum Institute, Washington, DC.
3. API Standard 660, *Shell-and-Tube Heat Exchangers*, American Petroleum Institute, Washington, DC.
4. *Steam—Its Generation and Use*, 40th Edition, Babcock & Wilcox, 1992.
5. *Combustion: Fossil Power Systems*, Third Edition, Combustion Engineering, Windsor, CT, 1981.
6. H. Thielsch, *Defects and Failures in Pressure Vessels and Piping*, Krieger Publishing, Malabar, FL, 1977.
7. R.D. Port and H.M. Herro, *The Nalco Guide to Boiler Failure Analysis*, McGraw-Hill, New York, NY, 1991.
8. D.N. French, *Metallurgical Failures in Fossil Fired Boilers*, John Wiley and Sons, New York, NY, 1993.
9. B. Dooley and W. McNaughton, *Boiler Tube Failures: Theory and Practice*, 3 Volumes, EPRI, 1995.



Figure 3-55-1—Short-term overheating failure of a vertical, 4.5-in. OD, schedule 160 2¼Cr-1Mo (SA335-P22) hydrocracker radiant tube that was 21 years old. Failure resulted from process-side starvation with the burners running.



Figure 3-55-2—Tube bulged and ruptured due to short-term overheating at a temperature well over 1380 °F (750 °C).



Figure 3-55-3—1Cr- $\frac{1}{2}$ Mo boiler superheater tube in 700 psig steam service that failed due to overheating.

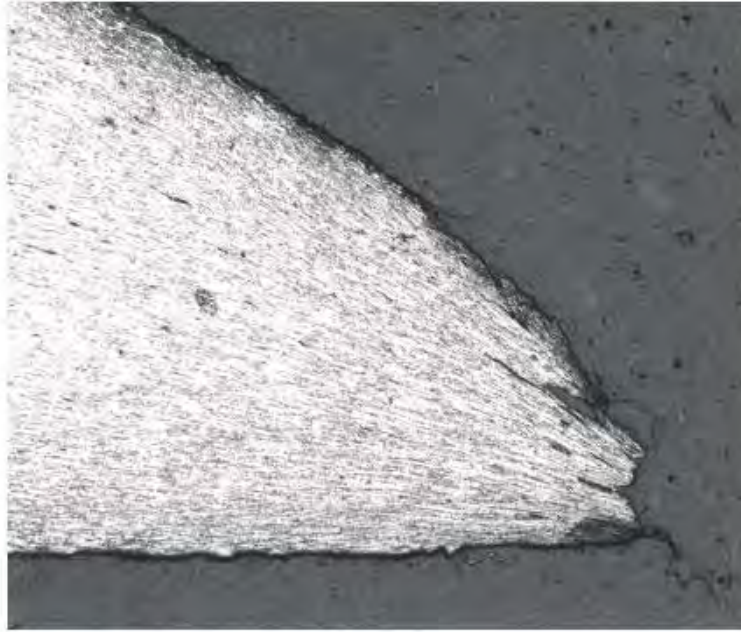


Figure 3-55-4—The fracture-edge microstructure displays severely elongated ferrite grains, proof of the ductility of the rupture. The thickness at the edge is about 0.01 in., which is a reduction in the wall thickness of more than 95 %. Magnification 50X, etched.



Figure 3-55-5—Short-term, high-temperature boiler tube failures from DNB are wide-open bursts with the failure lips drawn to a near knife edge. They are ductile ruptures. Magnification 25X.

3.56 Sigma Phase Embrittlement

3.56.1 Description of Damage

Formation of a metallurgical phase known as sigma phase in some stainless steels when they are heated above about 1000 °F (540 °C) can result in a loss of ductility and fracture toughness. The embrittlement can lead to cracking failure.

3.56.2 Affected Materials

- a) 300 series SS wrought metals, weld metal, and castings. Cast 300 series SS including the HK and HP alloys are especially susceptible to sigma formation because of their high (10 % to 40 %) ferrite content.
- b) 400 series SS and other ferritic and martensitic stainless steel with > 17 % Cr are also susceptible (e.g. Types 430 and 440).
- c) Duplex stainless steels.

3.56.3 Critical Factors

- a) Alloy composition, temperature, and time at temperature are the critical factors.
 - 1. In susceptible alloys, the primary factor that affects sigma phase formation is the time of exposure at elevated temperature.
- b) The metallurgical change is a precipitation of a hard, brittle intermetallic compound that can also render the material more susceptible to intergranular corrosion. The precipitation rate and amount increases with increasing chromium and molybdenum content.
- c) Sigma phase forms in ferritic (Fe-Cr), martensitic (Fe-Cr), austenitic (Fe-Cr-Ni), and duplex stainless steels when exposed to temperatures in the range of 1000 °F to 1700 °F (540 °C to 925 °C). Embrittlement can result by holding within or cooling through the transformation temperature range.
- d) Sigma forms most rapidly from the ferrite phase that exists in 300 series SS and duplex stainless steel weld deposits. It also readily forms in duplex stainless steel base metals due to their nominally 50 % ferrite phase. It can also form in 300 series SS base metal (austenite phase) but usually more slowly.
- e) Some 300 series SS can exhibit about 10 % to 15 % sigma phase. Cast austenitic stainless steels, which typically have a high ferrite content (up to 40 %), can develop considerably more sigma than wrought austenitic stainless steels, and may have very poor high-temperature ductility.
- f) Formation of sigma phase in austenitic stainless steel weld metals can occur in a few hours, as evidenced by the tendency for sigma to form in austenitic stainless steel weld overlay subjected to a PWHT at 1275 °F (690 °C) during the fabrication of heavy wall pressure vessels.
- g) The tensile strength and yield strength of sigmatized stainless steels increases slightly compared with solution annealed material. This increase in strength is accompanied by a reduction in ductility (measured by percent elongation and reduction in area) and a slight increase in hardness.
- h) Stainless steels with sigma can normally withstand operating stresses at operating temperatures but upon cooling below about 500 °F (260 °C) may show a complete lack of fracture toughness as measured in a Charpy impact test. Laboratory tests of embrittled weld metal have shown a complete lack of fracture toughness below 1000 °F (540 °C).
 - 1. Tests performed on sigmatized 300 series SS (304H) samples from FCC regenerator internals have shown that even with 10 % sigma formation (a large amount), the Charpy impact toughness was still 39 ft-lb (53 J) at 1200 °F (650 °C).

2. For the 10 % sigmatized specimen, the values ranged from 0 % ductility at room temperature to 100 % at 1200 °F (649 °C). Thus, although the impact toughness is reduced at high temperature, the specimens broke in a 100 % ductile fashion, indicating that the wrought material is still suitable at operating temperatures. (See e.g. [Figure 3-56-2](#).)

3.56.4 Affected Units or Equipment

- a) Common examples include stainless steel cyclones, piping ductwork, and valves in high-temperature FCC regenerator service.
- b) 300 series SS weld overlays and tube-to-tubesheet attachment welds can be embrittled during PWHT of the underlying Cr-Mo base metal.
- c) Stainless steel heater tubes are susceptible and can be embrittled.

3.56.5 Appearance or Morphology of Damage

- a) Sigma phase embrittlement is a metallurgical change that is not readily apparent, and can only be confirmed through metallographic examination ([Figure 3-56-3](#) to [Figure 3-56-5](#)) and impact testing ([Table 3-56-1](#) and [Table 3-56-2](#) and [Figure 3-56-1](#)).
- b) Damage due to sigma phase embrittlement appears in the form of cracking, particularly at welds or in areas of high stress or high restraint.
- c) Most cases of embrittlement are found in the form of cracking in both wrought and cast metals, including welds, during turnarounds, or during start-up or shutdown when the material is below about 500 °F (260 °C) and the effects of embrittlement are most pronounced.

3.56.6 Prevention/Mitigation

- a) The best way to prevent sigma phase embrittlement is to use alloys that are resistant to sigma formation or to avoid exposing the material to the embrittling temperature range.
- b) Because of the lack of fracture ductility at room temperature, care should be taken to avoid application of high stresses to sigmatized materials during a shutdown, as a brittle fracture could result.
- c) 300 series SS can be de-sigmatized by solution annealing at 1950 °F (1065 °C) for 4 hr followed by a water quench. However, this is not practical for most equipment.
- d) Sigma phase in welds is typically minimized by controlling the ferrite content, i.e. by specifying the allowable range of ferrite in the weld metal, e.g. in the range of 5 % to 9 % for Type 347 and somewhat less ferrite for Type 304. Limiting the maximum ferrite content minimizes sigma formation during service or fabrication. The minimum ferrite content is needed to minimize hot short cracking during welding.
- e) For stainless steel weld overlayed Cr-Mo components, the fabrication plan and sequence should attempt to minimize the exposure of the overlay to base metal PWHT temperatures wherever possible, particularly in highly stressed locations.

3.56.7 Inspection and Monitoring

This damage mechanism is very difficult to find and is also time dependent. Thus, it may take a while to develop in service. Online inspection is not applicable. Awareness of susceptible equipment can help direct inspection planning.

- a) Sigma phase formation and embrittlement can be detected by removing and lab testing a sample of the suspect material. Metallographic examination and/or impact testing can be used, as applicable.

- b) For duplex stainless steels, ECT has been reported to find sigma phase embrittlement, primarily due to the change in microstructure. However, this is highly dependent upon the methodology employed as well as the knowledge and experience of the equipment operator.
- c) FMR can be used to verify the presence of sigma phase in severe cases but normally will only assess the condition at the surface of the component, not the thru-wall extent of the damage.

3.56.8 Related Mechanisms

885 °F (475 °C) embrittlement (3.1).

3.56.9 References

1. API Recommended Practice 581, *Risk-Based Inspection Methodology*, American Petroleum Institute, Washington, DC.
2. *High Temperature Corrosion in Refinery and Petrochemical Service*, High Temperature Engineering Bulletin HTB-2, INCO, New York, NY, 1960.
3. L. Garverick, *Corrosion in the Petrochemical Industry*, ASM International, 1994, pp. 29 and 129–136.
4. R. Viswanathan, *Damage Mechanisms and Life Assessment of High-temperature Components*, ASM International, 1989.
5. *Metals Handbook—Desk Edition*, ASM International, Materials Park, OH.
6. J. Hau and A. Seijas, “Sigma Phase Embrittlement of Stainless Steel in FCC Service,” Paper No. 06578, *Corrosion/2006*, NACE International, Houston, TX.
7. API Recommended Practice 577, *Welding Inspection and Metallurgy*, American Petroleum Institute, Washington, DC.
8. C.N. McCowan T.A. Siewert, and D.L. Olson, *Stainless Steel Weld Metal: Prediction of Ferrite Content*, WRC Bulletin 342, Welding Research Council, Shaker Heights, OH, 1989.
9. E.L. Creamer et al., “Embrittlement of Type 347 Stainless Steel Weldments by Sigma Phase,” *Welding Research Supplement*, June 1969, pp. 239–244.
10. G. Psuj, T. Chady, and C.G. Camerini, “Eddy Current Transducer Dedicated for Sigma Phase Evaluation in Duplex Stainless Steel,” *Journal of Sensors*, Vol. 2012, 2012.
11. K. Doughten, D. Bauer, M. Rakos, and P. Domenico, “Non-destructive Testing of Duplex Stainless Steel,” *Stainless Steel World Americas Conference and Expo*, October 2012.
12. J. Hau, “Sigma Phase Embrittlement of Type 304H Stainless Steel After FCCU Service,” Paper No. 09140, *Corrosion/2017*, NACE International, Houston, TX.

Table 3-56-1—Data for Property Trends of Toughness vs Temperature

Test Temperature	304 SS 2 % Sigma		321 SS 10 % Sigma		304 SS 1 % Sigma		304 SS 2 % Sigma		347 SS 1 % Sigma	
	% of Impact	% Shear	% of Impact	% Shear	% of Impact	% Shear	% of Impact	% Shear	% of Impact	% Shear
70 °F (21 °C)	21	0	7	0	—	—	21	10	30	90
500 °F (260 °C)	38	25	10	20	—	—	—	—	100	100
900 °F (480 °C)	44	50	15	40	20	10	—	—	100	100
1200 °F (650 °C)	63	100	21	60	71	90	77	90	100	100

NOTE 1 Percent of impact is a comparison to original impact strength of non-embrittled materials.

NOTE 2 The results for 304 SS in columns one and four are for different heats of material under different exposure conditions and are intended to exemplify variability of embrittlement.

Table 3-56-2—Charpy V-notch (CVN) Impact Test Results, Absorbed Energy in Joules (ft-lb) from Reference 6

Refinery	Location	Years of Service	Sigma Phase Content (%)	Temperature	
				RT	Service
A	Base metal	17	4.0	85 (63)	145 (107)
A	Weld metal	17	8.7	37 (27)	100 (74)
B	Base metal	19	12.0	12 (9)	43 (32)
C	Base metal	13	1.5	35 (26)	75 (55)

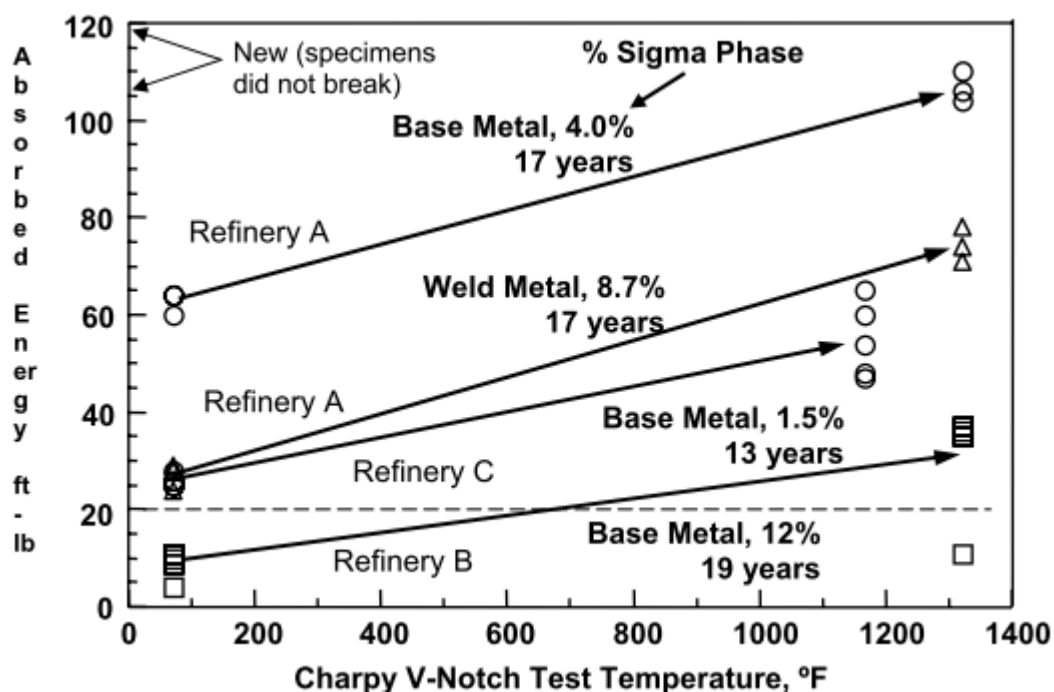


Figure 3-56-1—CVN impact test results as absorbed energy in ft-lb, at room temperature and service temperature. (Reference 6)

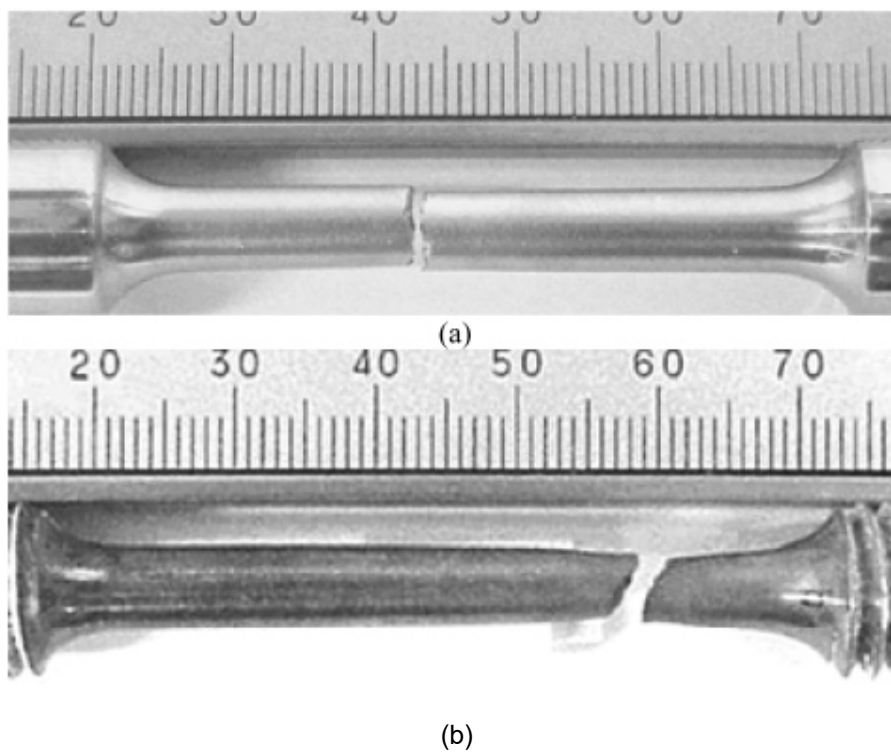


Figure 3-56-2—Tensile tests from 304H stainless steel FCC flue gas line with 12 % sigma phase. The top bar (a) failed in a brittle manner at room temperature. The bottom sample (b) was tested at the operating temperature and shows significant ductility and elongation at 1320 °F (716 °C). (Reference 6)

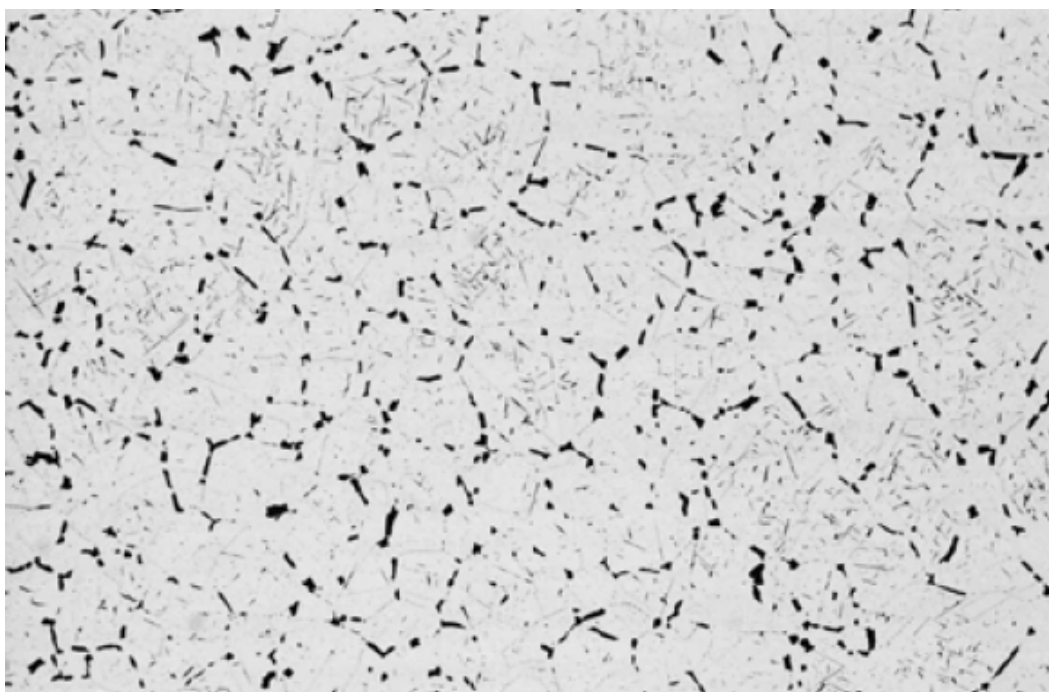


Figure 3-56-3—Microstructure of FCC regenerator plenum chamber wall, electrolytic etch in 33 % KOH, magnification 100X. Dark-etching particles are sigma phase; estimated amount is 6.0 %. (Reference 6)

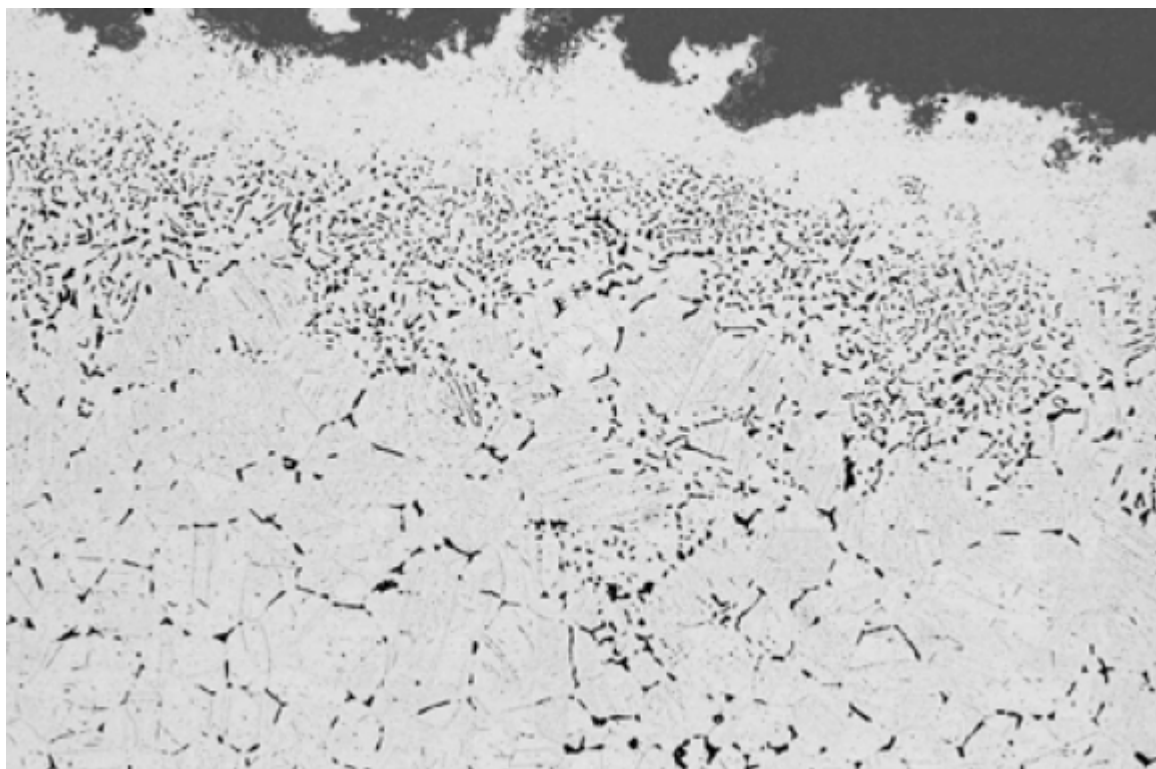
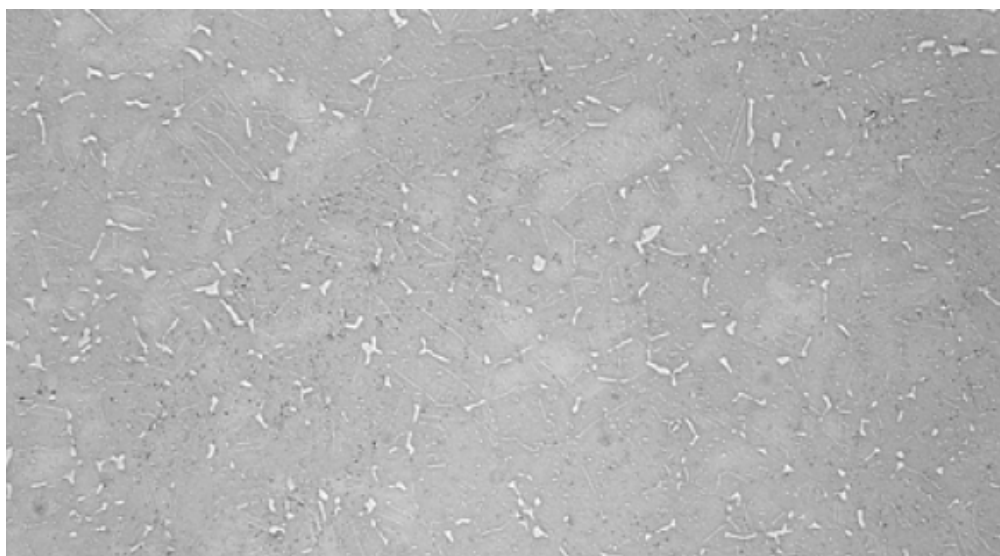
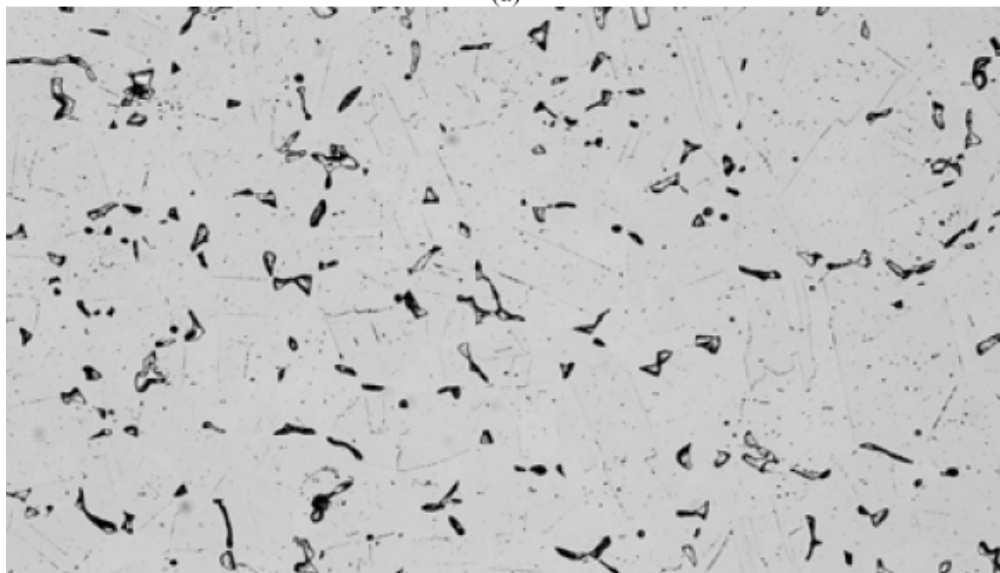


Figure 3-56-4—Dark-etching particles are sigma phase that are concentrated near the outside surface of FCC regenerator plenum chamber, electrolytic etch in 33 % KOH, magnification 100X. (Reference 6)



(a)



(b)

Figure 3-56-5—304H stainless steel with 14 years operation at a nominal temperature of 1320 °F (716 °C) after (a) etching in Vilella's reagent, magnification 100X, and (b) electrolytic etching in KOH, magnification 200X. The estimated amount of sigma phase was 5.0 %. (Reference 6)

3.57 Soil Corrosion

3.57.1 Description of Damage

The corrosion of metals from exposure to soils is referred to as soil corrosion.

3.57.2 Affected Materials

Carbon steel, cast iron, and ductile iron.

3.57.3 Critical Factors

- a) The severity of soil corrosion is determined by many factors, including operating temperature, moisture and oxygen availability, soil resistivity (soil condition and characteristics), soil type (water drainage capability) and homogeneity (variation in soil type), cathodic protection, stray current drainage, and coating type, age, and condition.
- b) There is no single parameter that can be used to determine soil corrosivity. Instead, a number of characteristics must be combined to estimate the corrosion in particular soil as outlined in ASTM STP 741 as well as API 580 and API 581.
- c) Soil resistivity is related to the soil moisture content and dissolved electrolytes in the soil water. Soil resistivity testing is frequently used to estimate soil corrosivity, mainly because it is easy to measure; however, it can produce widely variable results within a single refinery site.
- d) Soils having high moisture content, high dissolved salt concentrations, and high acidity are usually the most corrosive.
- e) Soil-to-air interface areas are often much more susceptible to corrosion than the rest of the structure because of moisture and oxygen availability. (Figure 3-57-1)
- f) Corrosion rates increase with increasing metal temperature.
- g) Other factors that affect soil corrosion include galvanic corrosion, dissimilar soils, stray currents, differential aeration corrosion cells, and MIC.

3.57.4 Affected Units or Equipment

- a) Underground piping and equipment as well as buried tanks and the bottoms of aboveground storage tanks. (Figure 3-57-2)
- b) Ground supported metal structures. (Figure 3-57-2)
- c) Piping running close to the ground under which soil has accumulated over the years to the point of reaching and contacting or partially covering the pipe.
- d) Piping exiting road or other crossings where soil has sloughed off and is laying on or covering the pipe.

3.57.5 Appearance or Morphology of Damage

- a) Soil corrosion appears as external thinning with a roughened surface and localized deeper attack or pitting.
- b) Poor condition of a protective coating is a tell-tale sign of potential corrosion damage.
- c) Soil corrosion can be highly variable along an unprotected buried pipe or on the unprotected underside of a storage tank bottom. (Figure 3-57-3)

3.57.6 Prevention/Mitigation

Soil corrosion of carbon steel can be minimized through the use of appropriate coatings and cathodic protection along with special backfill to prevent rock damage to the coating. The most effective protection is a combination of a corrosion-resistant coating and a cathodic protection system.

3.57.7 Inspection and Monitoring

The following techniques can be used for inspecting buried or on-grade metallic components that may have become covered by shifting soil, as well as soil-to-air interfaces.

- a) An aboveground visual survey can identify leaks coming to the surface of the soil.

NOTE Any change in the surface contour of the ground, discoloration of the soil, softening of paving asphalt, pool formation, bubbling water puddles, or noticeable odor.

- b) Smart-pigging devices employing UT or MFL can be used where the piping is designed to send and receive the pigs or accommodate tethered pigs that can be sent through lines. It can detect dents, flaws, and corrosion.
- c) A close-interval potential survey on a cathodically protected line may be used to verify that the buried piping has a protective potential throughout its length. API 570 provides guidance for conducting close-interval surveys. Close-interval potential surveys can only infer wall loss from CP potential, but not directly detect presence of wall loss, and thus they identify areas for follow-up inspection. Refer to NACE SP0169 and API 651 Section 11 of for guidance applicable to inspecting and maintaining cathodic protection systems for buried and soil-contacting equipment.
- d) A pipe coating holiday survey (e.g. direct current voltage gradient) can be used to locate coating defects on coated pipes. This can be performed on newly coated pipe before being buried or on pipe that has been excavated.
- e) VT of the pipe or equipment coating after excavation is one of the most reliable methods to determine its condition. This is also commonly done at the soil-to-air interface, where the soil should be removed down to about 12 in. (305 mm) below the surface to expose the most corrosion-prone area. Care should be taken during excavation to avoid damaging the coating or the equipment. Risks of excavating pipe while in service should be evaluated.
- f) GWT can provide a screening tool for metal loss on buried piping, but signal loss can limit the distance from the GWT collar over which the piping can be inspected.
- g) Pressure testing can determine whether buried equipment is leaking at that particular time but does not provide information concerning the degree of corrosion on the equipment.

3.57.8 Related Mechanisms

Galvanic corrosion (3.31), concentration cell corrosion (3.19), graphitic corrosion (3.33), and MIC (3.45).

3.57.9 References

1. API Recommended Practice 580, *Risk-Based Inspection*, American Petroleum Institute, Washington, DC.
2. API Recommended Practice 581, *Risk-Based Inspection Methodology*, American Petroleum Institute, Washington, DC.
3. A.W. Peabody, *Control of Pipeline Corrosion*, NACE International, Houston, TX, 1967.
4. J. Morgan, *Cathodic Protection*, NACE International, Houston, TX, 1987.

5. D.K. O'Day, "External Corrosion in Distribution Systems," *Journal AWWA*, Vol. 81, No. 10, October 1989, pp. 45–52.
6. M.E. Parker, *Pipe Line Corrosion and Cathodic Protection*, Gulf Publishing Company, Houston TX, 1954.
7. M. Romanoff, *Underground Corrosion*, NACE International, Houston, TX, 1997.
8. D.A. Jones, *Principles and Prevention of Corrosion*, McMillan, New York, NY, 1992.
9. H.H. Uhlig, *Corrosion Handbook*, John Wiley and Sons, 1948.
10. EDM Services, *Hazardous Liquid Pipeline Risk Assessment*, California State Fire Marshal, Pipeline Safety Division, Simi Valley, CA, 1993.
11. NACE SP0169, *Control of External Corrosion on Underground or Submerged Metallic Piping Systems*, NACE International, Houston, TX.



Figure 3-57-1—Corrosion of carbon steel pipe at the soil/air interface where the pipe emerges from underground.



Figure 3-57-2—Coupons removed from the bottom of an unprotected steel condensate storage tank after 3 years of service. The external surface is shown.

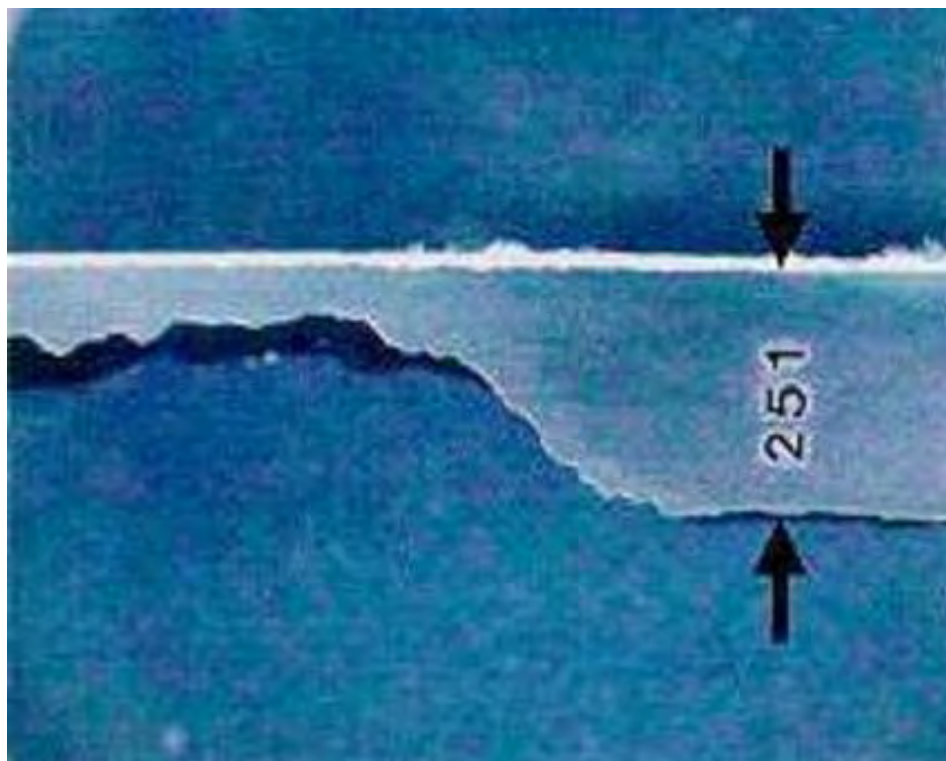


Figure 3-57-3—Cross section through location (A) showing severe corrosion. The arrows point to a location that was at the original thickness.

3.58 Sour Water Corrosion (Acidic)

3.58.1 Description of Damage

- a) Corrosion of steel (primarily) due to acidic sour water (SW) containing H_2S at a pH between 4.5 and 7.0. Carbon dioxide (CO_2) may also be present as well as other acidic species such as dissolved organic acids.
- b) SWs containing significant amounts of ammonia, chlorides, or cyanides, which may significantly affect pH, are outside the scope of this section.

3.58.2 Affected Materials

- a) Primarily affects carbon steel.
- b) Stainless steels, copper alloys, and nickel-based alloys are usually resistant.

3.58.3 Critical Factors

- a) H_2S content, pH, temperature, velocity, and oxygen concentration are all critical factors.
- b) The H_2S concentration in the SW is dependent on the H_2S partial pressure in the gas phase as well as temperature and pH.
- c) At a given pressure, the H_2S concentration in the SW decreases as temperature increases.
- d) Increasing concentrations of H_2S tend to decrease solution pH down to about 4.5. Streams with a pH below 4.5 indicate the presence of a strong acid, which would be the main corrosion concern.
- e) Above a pH of about 4.5, a protective, thin, iron sulfide layer helps limit the corrosion rate.
- f) In some instances, at a pH above 4.5, a thicker, porous sulfide film layer can form. This can promote pitting under the sulfide deposits.
- g) Other contaminants have a significant effect on water pH. For example, HCl and CO_2 reduce the pH (make it more acidic). Ammonia significantly increases pH and is more often associated with alkaline SW where the main concern is ammonium bisulfide corrosion. (See [3.5](#).)
- h) The presence of air or oxidants may increase the corrosion rate and usually produces pitting or under-deposit attack.

3.58.4 Affected Units or Equipment

Acidic SW corrosion is a concern in overhead systems of FCC and coker gas fractionation plants with high H_2S levels and low NH_3 levels.

3.58.5 Appearance or Morphology of Damage

- a) Corrosion damage from acidic SW is typically general thinning. However, localized corrosion or localized under-deposit attack can occur, especially if air or oxygen is present. (Corrosion in high- CO_2 environments caused primarily by the CO_2 is covered in [3.18](#).)
- b) 300 series SS is susceptible to pitting attack and may experience crevice corrosion and/or Cl^- SCC. (See [3.17](#).)

3.58.6 Prevention/Mitigation

- a) Process monitoring and control are important for minimizing the effects of acidic SW corrosion. Process parameters that typically should be monitored, e.g. at water draws of overhead accumulators, and controlled where applicable, are as follows:
1. H_2S content,
 2. pH,
 3. chloride content,
 4. cyanide content,
 5. temperature,
 6. fluid velocity, and
 7. oxygen concentration.
- b) 300 series SS can be used at temperatures below about 140 °F (60 °C) where Cl^- SCC is not likely.
- c) Copper alloys and nickel alloys are generally not susceptible to acid SW corrosion. However, copper alloys are vulnerable to corrosion and some are susceptible to SCC in environments with ammonia.
- d) Water wash injection into FCC overheads and coker light ends units dissolves and dilutes corrodents like H_2S and cyanide (CN^-). Additional injection of a polysulfide solution with the water wash helps to convert cyanides into a less harmful compound.

3.58.7 Inspection and Monitoring

- a) UT scanning and RT can identify locally thinned areas of equipment exposed to SW corrosion.
- b) Permanently mounted thickness monitoring sensors can be used.
- c) Strategically placing continuous corrosion monitoring in the system, e.g. corrosion probes, corrosion coupons, or online thickness monitoring sensors, can provide an early indication of increased corrosion rates and the need to conduct thickness surveys or apply more advanced NDE to verify the severity and extent of the indicated corrosion.

NOTE Corrosion probes may provide misleading data due to formation of FeS scale on the probe.

- d) Process monitoring and control, as described in 3.58.6 above, are key to controlling acidic SW corrosion and helping identify areas that should be included in the inspection plan.

3.58.8 Related Mechanisms

Other damage mechanisms to consider in these environments include wet H_2S damage (3.67) and CO_2 corrosion (3.18). See also ammonium bisulfide corrosion (3.5) and concentration cell corrosion (3.19).

3.58.9 References

1. J. Gutzeit, "Corrosion of Steel by Sulfides and Cyanides in Refinery Condensate Water," *Materials Protection*, December 1968, pp. 17–23.
2. R.H. Hausler and N.D. Coble, "Corrosion Control in Crude Unit Overhead Systems," Paper 42-72, *API 37th Midyear Meeting*, May 1972.

3. B.D. Craig, "The Nature of Sulfides Formed on Steel in an H₂S-O₂ Environment," *CORROSION*, Vol. 35, No. 3, March 1979, p. 136–138.
4. C.P. Dillon, *Corrosion Control in the Chemical Process Industries*, Materials Technology Institute (printed by NACE), MTI Publication No 45, Second Edition, St. Louis, MO, 1994.
5. D.A. Jones, *Principles and Prevention of Corrosion*, Prentice-Hall, New York, NY, 1996.
6. B.D. Craig, "Sour-gas Design Considerations," *Society of Petroleum Engineers (SPE) Monograph Series*, Monograph Volume 15, 1993.

3.59 Spheroidization (Softening)

3.59.1 Description of Damage

Spheroidization is a change in the microstructure of steels resulting from exposure in the 850 °F to 1400 °F (440 °C to 760 °C) range, where the carbide phases in carbon steels and C-½Mo steels are unstable and may agglomerate from their normal plate-like form to a spheroidal form or from small, finely dispersed carbides in Cr-Mo steels to large agglomerated carbides. Spheroidization may cause a loss in strength and/or creep resistance.

3.59.2 Affected Materials

All commonly used grades of carbon steel and low-alloy steels including C-½Mo, 1Cr-½Mo, 1¼Cr-½Mo, 2¼Cr-1Mo, 3Cr-1Mo, 5Cr-½Mo, and 9Cr-1Mo steels.

3.59.3 Critical Factors

- a) Metal chemical composition, microstructure, exposure time, and temperature are critical factors.
- b) The rate of spheroidization depends on the temperature and initial microstructure. Spheroidization can occur in a few hours at 1300 °F (550 °C) but may take several years at 850 °F (455 °C).
- c) Annealed steels are more resistant to spheroidization than normalized steels. Coarse-grained steels are more resistant than fine grained. Fine-grained silicon-killed steels are more resistant than aluminum killed.

3.59.4 Affected Units or Equipment

- a) Spheroidization can occur in piping and equipment after exposure to temperatures above 850 °F (455 °C). The loss in strength may be as high as about 30 %, but failure is not likely to occur except under very high applied stresses, in areas of stress concentration, or in combination with other damage mechanisms.
- b) The loss in strength is usually accompanied by an increase in ductility, which allows for deformation at stress concentrations.
- c) Spheroidization affects hot-wall piping and equipment in the FCC, catalytic reforming, and coker units. Fired boiler tubes and fired heater tubes in process units may be affected by a loss in creep strength, but equipment is seldom renewed or repaired because of spheroidization.

3.59.5 Appearance or Morphology of Damage

- a) Spheroidization is not visible or readily apparent and can only be observed through metallography. In carbon steel, the pearlite phase undergoes a time-dependent transformation from partial to complete spheroidization. (Figure 3-59-1 and Figure 3-59-2)
- b) In the case of the 5 % to 9 % Cr-Mo alloys, spheroidization is the process of transforming the carbides from their original finely dispersed morphology to large agglomerated carbides.

3.59.6 Prevention/Mitigation

Spheroidization is difficult to prevent except by minimizing long-term exposure to elevated temperatures.

3.59.7 Inspection and Monitoring

- a) Spheroidization is primarily found using FMR or removal of samples for metallographic evaluation.
- b) Because spheroidization may result in a reduction in tensile strength (and therefore, hardness), field hardness testing may indicate the presence of spheroidization, but it should be followed up with sampling and/or FMR to confirm its existence.

3.59.8 Related Mechanisms

Closely related to graphitization (3.34). Spheroidization and graphitization are competing mechanisms that occur at overlapping temperature ranges. At temperatures above about 1025 °F (550 °C), graphitization may occur after spheroidization. Below 1025 °F (550 °C), graphitization occurs before the steel is fully spheroidized.

3.59.9 References

1. *ASM Handbook—Properties and Selection: Iron, Steels, and High-performance Alloys*, Volume 1, ASM International, Materials Park, OH.
2. D.N. French, "Microstructural Degradation," The National Board of Boiler and Pressure Vessel Inspectors, <http://www.nationalboard.com>, June 2001.
3. R.D. Port, "Non-weld-related Graphitization Failures," Paper No. 248, *Corrosion/89*, NACE International, Houston, TX.

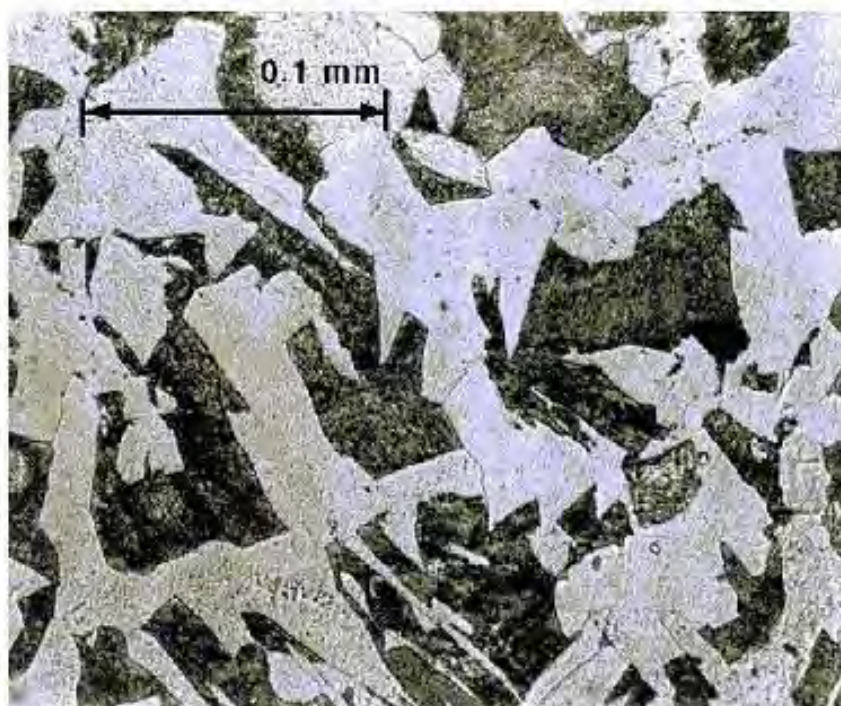


Figure 3-59-1—High-magnification photomicrograph of metallographic sample showing typical ferrite-pearlite structure of carbon steel.

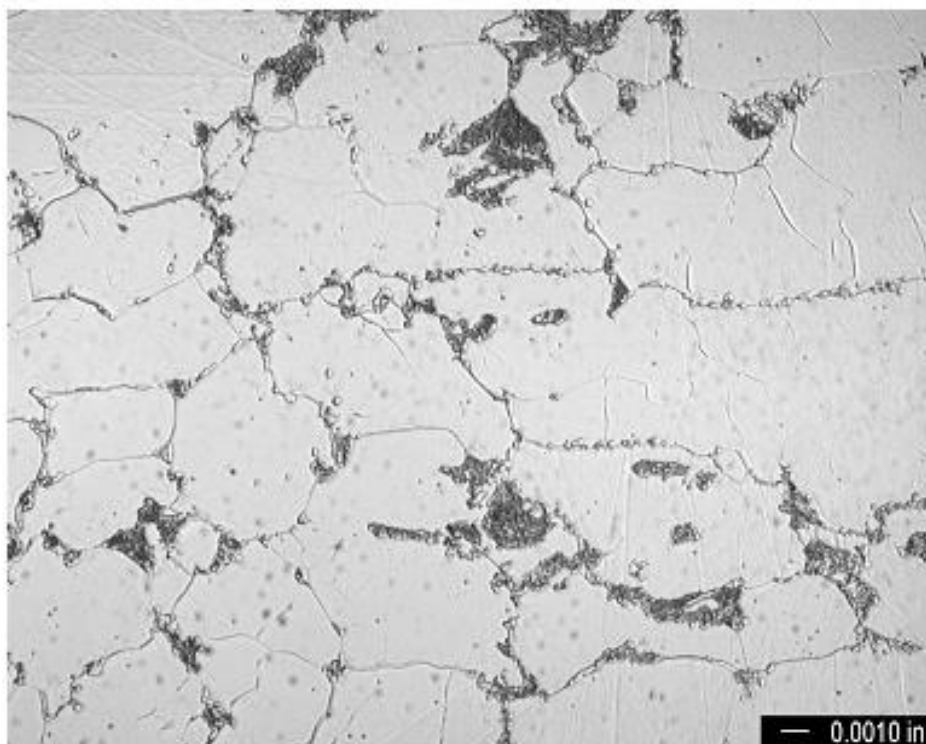


Figure 3-59-2—High-magnification photomicrograph of metallographic sample showing spheroidized carbides.

3.60 Strain Aging

3.60.1 Description of Damage

Strain aging is a form of metallurgical damage found mostly in older (pre-1980) carbon steels and C- $\frac{1}{2}$ Mo low-alloy steels that were not fully deoxidized as more modern steels are. It is associated with older steel-making processes such as the Bessemer and open hearth processes, which use air instead of oxygen to remove carbon. Strain aging occurs in a susceptible steel under the combined effects of deformation and aging at an intermediate temperature. This results in an increase in hardness and strength with a reduction in ductility and toughness. Strain aging is a concern because it increases the chances of brittle fracture.

3.60.2 Affected Materials

Mostly older (pre-1980) carbon steels with a large grain size and C-0.5 Mo low-alloy steel.

3.60.3 Critical Factors

- a) Steel composition and manufacturing process determine steel susceptibility.
- b) Steels manufactured by the Bessemer or open hearth process, both of which use air to remove carbon, contain a higher level of nitrogen than newer steels manufactured by the basic oxygen furnace process.
- c) In general, steels made by the basic oxygen furnace process and fully killed (deoxidized) with aluminum will not be susceptible. The effect is found in steels with higher levels of nitrogen and carbon, but not in the modern fully deoxidized carbon steels.
- d) Strain aging effects are observed in materials that have been cold worked and placed into service at intermediate temperatures without stress relieving.
- e) Strain aging is a major concern for equipment that contains cracks. If susceptible materials are plastically deformed and exposed to intermediate temperatures, the zone of deformed material may become hardened and less ductile. This phenomenon has been associated with several vessels that have failed by brittle fracture, typically following repair welds that were not PWHT'd.
- f) The pressurization sequence vs temperature is a critical issue to prevent brittle fracture of susceptible equipment.
- g) Strain aging can also occur when welding susceptible materials, especially in areas near stress concentrations, at closely spaced welds, or in repairs. When strain aging occurs during the welding cycle as a result of the combined effects of the heat of welding and residual welding stresses, it has been termed dynamic strain aging.

3.60.4 Affected Units or Equipment

Strain aging is most likely to occur in thick wall vessels manufactured from susceptible materials that have not been stress relieved.

3.60.5 Appearance or Morphology of Damage

Strain aging can be revealed through detailed metallurgical analyses, but damage most likely will not be identified as strain aging until fracture has already occurred. In cases where strain aging results from metal forming at ambient temperature and then aging at an intermediate temperature in service, the effects of strain aging have been observed by an increase in the hardness.

3.60.6 Prevention/Mitigation

- a) Strain aging is not an issue for newer steels that contain low levels of interstitial impurity elements and sufficient aluminum (>0.015 wt %) to fully deoxidize the steel.

- b) For older equipment, extra care should be taken to avoid the potentially damaging effects of strain aging by avoiding stressing or pressurizing equipment until the metal temperature reaches an acceptable level where the risk of brittle fracture is low. Refer to curve "A" in UCS 66 of the ASME *BPVC* Section VIII, Division 1 for pressurization temperatures of vessels susceptible to strain aging effects.
- c) Applying PWHT to weld repairs of susceptible materials will eliminate the effects of strain aging, because heating in the temperature range of 1100 °F to 1200 °F (595 °C to 650 °C) eliminates the strain that causes the embrittlement. Where PWHT is not possible, buttering should be considered to minimize welding residual stresses acting on the old material being welded.

3.60.7 Inspection and Monitoring

- a) There are no commercially available online inspection or monitoring techniques to detect strain aging.
- b) Hardness testing can be used in cases where strain aging has occurred over a large area of the material. Hardness testing is not effective in detecting strain aging embrittlement resulting from welding.

3.60.8 Related Mechanisms

When deformation occurs at the intermediate temperature, as is the case of welding, the mechanism is referred to as dynamic strain aging. Blue brittleness is another form of strain aging.

3.60.9 References

1. ASME *Boiler and Pressure Vessel Code*, Section VIII, Division 1, American Society of Mechanical Engineers, New York, NY.

3.61 Sulfidation

3.61.1 Description of Damage

Corrosion of carbon steel and other alloys resulting from their reaction with sulfur compounds in high-temperature environments. Corrosion in the presence of hydrogen is discussed in 3.35, *High-temperature H₂/H₂S Corrosion*. In this discussion, sulfidation will refer to high-temperature sulfidic environments without hydrogen. This mechanism is also known as sulfidic corrosion. Because of the smooth, large, relatively uniformly corroded surface produced by sulfidation, it can lead to rupture type failure rather than a localized or pinhole leak. Both types of sulfidation, with and without hydrogen present, are covered in much more detail in Reference 6 (API 939-C).

3.61.2 Affected Materials

- a) All iron-based materials including carbon steel and low-alloy steels, 400 series SS, and 300 series SS, in that order from most susceptible to less susceptible.
- b) Nickel-based alloys are also affected to varying degrees depending on composition, especially chromium content. Above 1193 °F (645 °C), alloys containing high nickel contents can suffer a form of sulfidation and metal loss associated with the formation of nickel sulfides beneath the metal surface. This has also been referred to as hot corrosion. Susceptibility to this form of sulfidation increases with increasing nickel content.
- c) Copper-based alloys form sulfide corrosion product at lower temperatures than carbon steel.

3.61.3 Critical Factors

- a) Major factors affecting sulfidation are chemical composition of the metal, temperature, and concentration of corrosive (reactive) sulfur compounds. Flow conditions can also affect the rate of damage.
- b) In general, the resistance of iron-based and nickel-based alloys is determined by the chromium content of the material. Increasing the chromium content significantly increases resistance to sulfidation. 300 series SS, such as Types 304, 316, 321, and 347, are highly resistant in most refining high-temperature sulfidation process environments. Nickel-based alloys are similar to stainless steels in that similar levels of chromium provide similar resistance to sulfidation; however, nickel alloys with little or no chromium can have poor resistance to these environments.
- c) Figure 3-61-1 and Figure 3-61-2 show the typical effects of increasing chromium content, temperature, and sulfur content on metal loss. These curves only indicate the general trends in the effects of chemical composition, temperature, and sulfur content on corrosion rates. They are used in design for estimating the corrosion rate for a particular service but should be regarded as only showing trends, as actual observed rates can often vary substantially. In many cases the predictions are conservative, i.e. they overstate the actual corrosion rates found in service. The references at the end of this section provide additional background on the development of these curves.
- d) The silicon content of carbon steel can significantly affect its susceptibility to sulfidation. Carbon steels with Si content less than 0.10 % have been found to suffer variable and often higher sulfidation corrosion rates than carbon steel with silicon content above this level. (Higher-Si carbon steels are still susceptible to sulfidation, but steel with low Si content may suffer higher rates.) Silicon-killed steel has greater than 0.10 % Si, while non-killed steels generally do not. There have been a number of incidents in the refining industry where lower-Si ASTM Grade A53 piping suffered significantly more metal loss than ASTM Grade A106 piping or standard carbon steel pipe fittings or flanges welded to the A53 pipe.
- e) The amount of metal loss suffered in a particular service is greatly affected by the material's ability to form a protective sulfide scale. While sulfide scale invariably forms as a corrosion product on the metal surface, the degree to which it is protective depends on its thickness, density, adherence, and completeness of coverage, which depend on its chemical composition and the severity of the process stream, including flow regime.

- f) Sulfidation (H_2 -free) of iron-based alloys begins at metal temperatures above 450 °F (230 °C) but normally only becomes a practical concern above 500 °F (260 °C). Experience has shown 500 °F (260 °C) to be the most useful service temperature above which to focus inspection, monitoring, and corrosion mitigation efforts.
- g) Crude oils and other hydrocarbon streams contain sulfur compounds at various concentrations. Total sulfur content is made up of many different sulfur or sulfide species.
- h) Sulfidation is primarily caused by H_2S and other reactive sulfide species formed by the thermal decomposition of sulfur compounds at high temperatures. Some sulfur compounds react more readily to form H_2S . Therefore, it can be misleading to predict corrosion rates based on weight percent of sulfur alone. Knowing the total “reactive sulfur” in the process stream is key to predicting or assessing its actual corrosivity.

3.61.4 Affected Units or Equipment

- a) Sulfidation occurs in piping and equipment in high-temperature environments where sulfur-containing liquid, vapor, or mixed streams are processed.
- b) Crude, vacuum, FCC, coker, and visbreaker units, as well as the feed sections of hydroprocessing units upstream of hydrogen injection [at which point high-temperature H_2/H_2S corrosion (3.35) begins to govern], commonly process these high-temperature, sulfur-containing streams without, or prior to, intentionally added hydrogen.
- c) Coker heaters fabricated from higher-nickel alloys such as Alloy 800H have shown accelerated sulfidation corrosion rates in the lower radiant sections operating with tube metal temperatures exceeding 1193 °F (645 °C) as compared to similar tubes operating below this temperature.
- d) Heaters fired with oil, gas, coke, and most other sources of fuel may be affected depending on sulfur levels in the fuel; it is now uncommon for heaters to be fired with anything but gas, usually low-sulfur gas to meet environmental restrictions, especially in the United States.

3.61.5 Appearance or Morphology of Damage

- a) Depending on service conditions, corrosion is most often in the form of uniform thinning but can also occur as localized corrosion or high-velocity erosion-corrosion damage. (Figure 3-61-3 to Figure 3-61-7)
- b) While generally having a uniform thinning morphology, the amount of thinning can vary at different locations in the system or at different locations along the length of a piping run.
 - 1. The difference in the degree of thinning between low-Si (<0.10 % Si) pipe and higher-Si (≥0.10 Si) pipe in the same system can be large, with a marked step change in remaining wall thickness at the transition. See Figure 3-61-4 and Figure 3-61-5.
- c) A sulfide scale will usually cover the surface of components. Deposits may be thick or thin depending on the alloy, corrosiveness of the stream, and fluid flow regime and velocity.

3.61.6 Prevention/Mitigation

- a) Resistance to sulfidation is generally achieved by upgrading to a higher-chromium steel such as 9Cr-1Mo.
- b) Piping and equipment constructed from solid or clad (or overlaid) 300 series SS should provide significant resistance to corrosion. 400 series SS cladding should also provide significant improvement over carbon steel. Solid 400 series SS is generally not selected for piping or other pressure-containing equipment because of embrittlement and fracture toughness concerns.
- c) Aluminum diffusion treatment of carbon steel and low-alloy steel components is sometimes used to reduce sulfidation rates and minimize scale formation; however, it may not offer complete protection.

- d) For operation above 1193 °F (645 °C), sulfidation rates of higher-nickel alloys can be reduced by selecting an alloy with a lower Ni content.

3.61.7 Inspection and Monitoring

- a) Thinning in piping, tubing, and other equipment can be detected and measured using UT thickness measurement or RT. Thinning in pressure vessels and large-diameter piping where internal inspection is possible can be detected by internal VT, typically followed up with UT.
- b) Permanently mounted thickness monitoring sensors can be used.
- c) Thinning in heater tubes can be detected using UT or by smart pigging. Smart pigging provides significantly more coverage than spot UT and may find thinning missed by spot UT.
- d) Actual operating temperatures should be verified and compared against design. Temperatures and sulfur levels should be monitored for increases above design.
- e) Temperatures can be monitored using tube-skin thermocouples and/or infrared thermography.
- f) Proactive and retroactive MVPs (materials verification programs) can be used for alloy verification and to check for alloy mix-ups in services where sulfidation is anticipated. (API 578 provides guidance on MVPs.) See [Figure 3-61-6](#).
- g) Most refiners have instituted programs to identify low-Si carbon steel piping or components in sulfidation service by measuring the thickness of components in vulnerable piping systems. A small number of refiners have followed a PMI-type approach to measuring or otherwise determining the Si content of piping components.

3.61.8 Related Mechanisms

Sulfidation is also known as sulfidic corrosion. High-temperature sulfidation in the presence of hydrogen is covered in [3.35](#).

3.61.9 References

1. H.F. McConomy, "High Temperature Sulfidic Corrosion in Hydrogen-free Environments," *API Proceedings*, Vol. 43(III), 1963, pp. 78–96.
2. J. Gutzeit, "High Temperature Sulfidic Corrosion of Steels," *Process Industries Corrosion—The Theory and Practice*, NACE International, Houston, TX, 1986, pp. 171–189.
3. J. Gutzeit, R.D. Merrick, and L.R. Scharfstein, "Corrosion in Petroleum Refining and Petrochemical Operations," *Metals Handbook*, Volume 13, ASM International, Materials Park, OH, 1987, pp. 1262–1287.
4. E.B. Backenstow et al., "High Temperature Hydrogen Sulfide Corrosion," *CORROSION*, Vol. 12, No. 1, 1956, pp. 6t–16t.
5. NACE Task Group 176 Draft Report, "Overview of Sulfidic Corrosion in Petroleum Refining," NACE International, Houston, TX, 2003.
6. API Recommended Practice 939-C, *Guidelines for Avoiding Sulfidation (Sulfidic) Corrosion Failures in Oil Refineries*, American Petroleum Institute, Washington, DC.
7. API Recommended Practice 578, *Guidelines for a Material Verification Program (MVP) for New and Existing Assets*, American Petroleum Institute, Washington, DC.

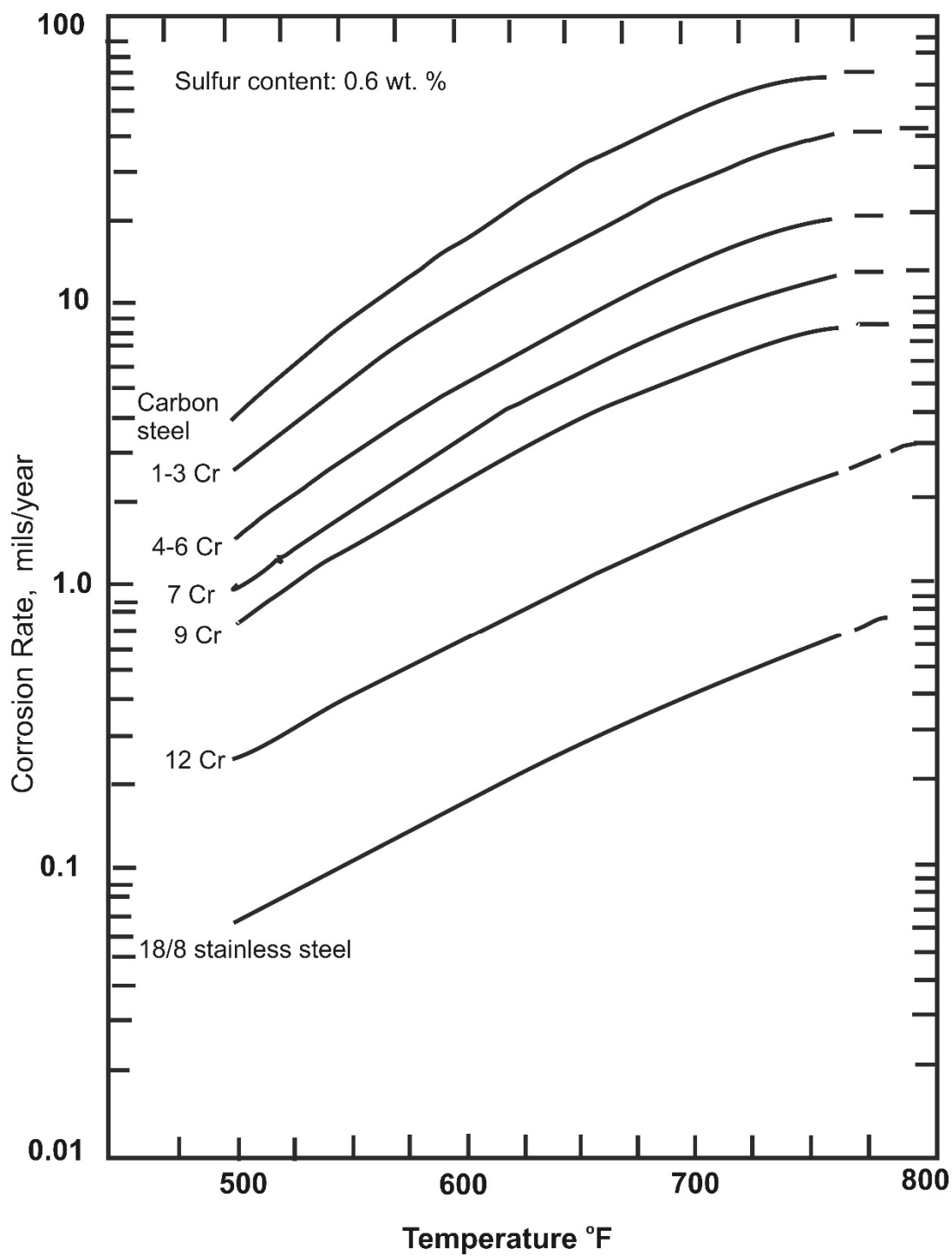


Figure 3-61-1—Modified McCconomy curves showing typical effect of temperature on high-temperature sulfidation of steels and stainless steels. (Reference 3)

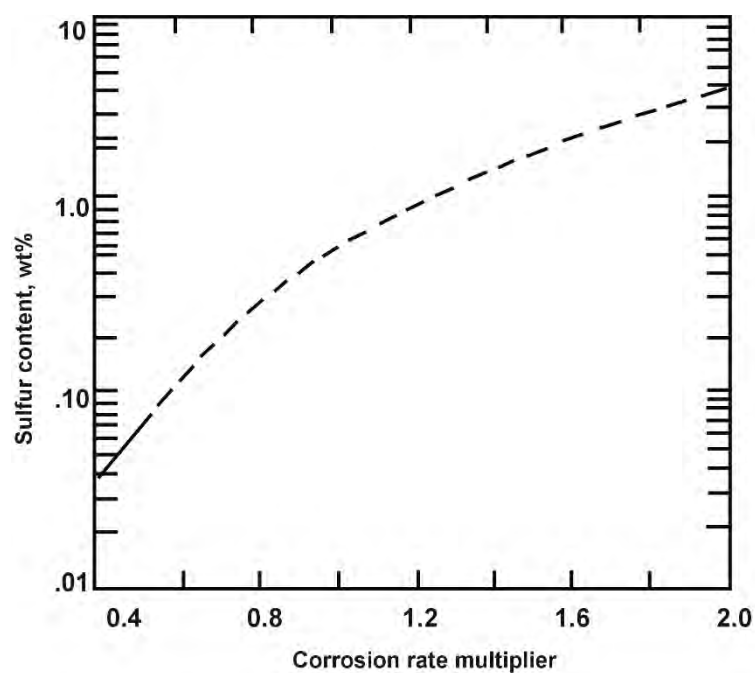


Figure 3-61-2—Multiplier for corrosion rates in Figure 3-61-1 based on the sulfur content of process fluid. (Reference 3)



Figure 3-61-3—Sulfidation failure of an 8-in. carbon steel pipe. Note the relatively uniform thinning that resulted in a sizeable rupture.



Figure 3-61-4—Sulfidation failure illustrating the effect of accelerated corrosion due to low silicon content. This 8-in. pipe section in FCC bottoms piping was in service at 150 psig (1 Mpa) at 650 °F to 700 °F (340 °C to 370 °C). The piping sketch in Figure 3-61-5 illustrates the difference in corrosion rate as compared to adjacent high-silicon components.

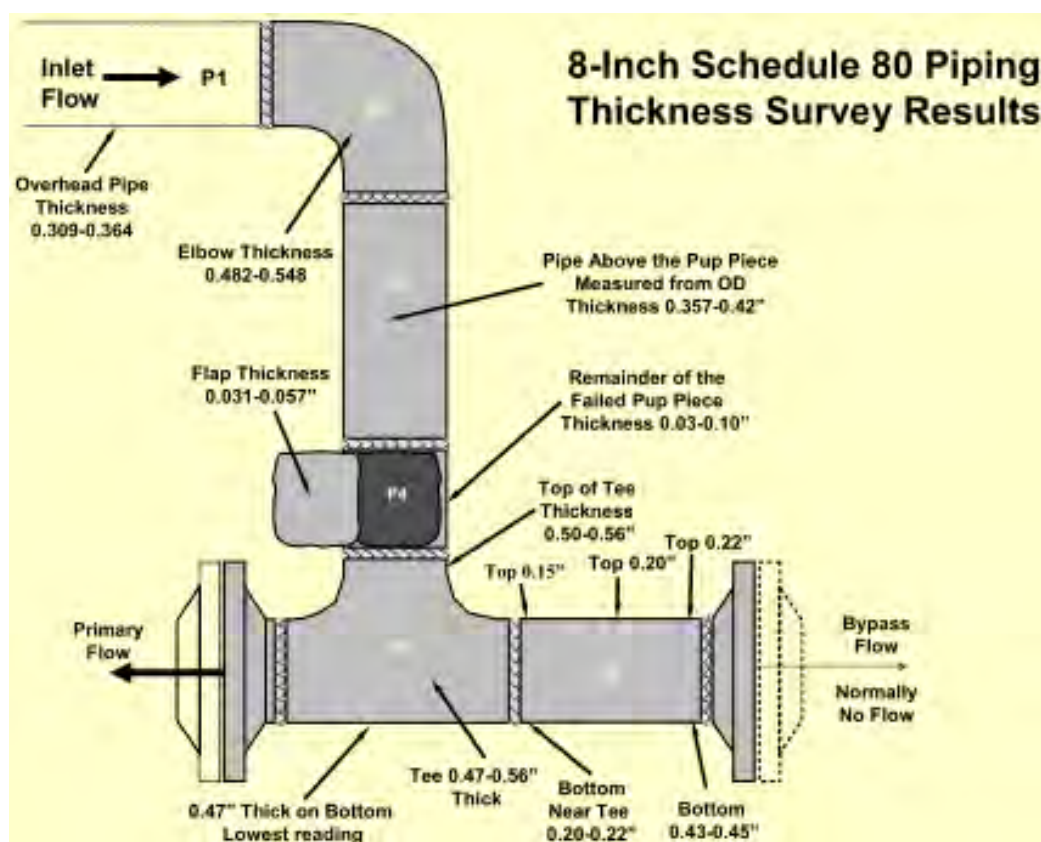


Figure 3-61-5—Thickness survey of 8-in. pipe shown in Figure 3-61-4 above.



Figure 3-61-6—Sulfidation failure of a carbon steel sight glass nipple on the right after 2 years in a crude unit. Original thickness is shown on left for comparison. Material was supposed to be 9Cr-1Mo.



Figure 3-61-7—Sulfidation failure of piping elbow.

3.62 Sulfuric Acid Corrosion

3.62.1 Description of Damage

Sulfuric acid promotes general and localized corrosion of carbon steel and other alloys. Carbon steel HAZs may experience accelerated corrosion.

3.62.2 Affected Materials

In order of increasing resistance: carbon steel, 316L SS, Alloy 20, high-silicon cast iron, high-nickel cast iron, Alloy B-2, and Alloy C-276.

3.62.3 Critical Factors

- a) Acid concentration, temperature, alloy content, velocity, contamination, and presence of oxidizers.
- b) [Figure 3-62-1](#) shows a plot of carbon steel corrosion rates as a function of sulfuric acid concentration and temperature.
- c) Corrosion of steel by dilute acid is usually in the form of overall metal loss or pitting and becomes more severe with increasing temperature and velocity.
- d) Carbon steel corrosion rates increase significantly if the flow velocity exceeds about 2 fps to 3 fps (0.6 m/s to 0.9 m/s) or at acid concentrations below 65 %, since these conditions reduce the ability to maintain a protective ferrous sulfate scale.
- e) Under stagnant or low-flow conditions [<0.5 fps (<0.15 m/s)], a mechanism known as hydrogen grooving can occur where movement of hydrogen bubbles on the steel surface removes the protective film and locally increases the corrosion rate. It is essentially an erosion-corrosion mechanism. Hydrogen grooving can cause corrosion along the sides and top of piping and equipment.
- f) Mix points where acid is mixed with neutral or alkaline water cause heat to be released, with the resulting elevated temperature causing an acceleration of the corrosion rate. High corrosion rates can also occur where concentrated acid becomes diluted.
- g) The presence of oxidizers (e.g. oxygen) or contaminants (e.g. iron) can greatly increase the corrosion rate, especially for Alloy B-2.
- h) Stainless steel performance can be similar to carbon steel, especially in <92 % H_2SO_4 or at elevated temperatures. The addition of Mo to 300 series SS can improve corrosion resistance in <92 % H_2SO_4 , but performance is still unpredictable due to the ability of the acid to act as either a reducing acid or an oxidizing acid depending on concentration and contaminants.

3.62.4 Affected Units or Equipment

- a) Sulfuric acid alkylation units and waste water treatment plants are affected.
- b) Areas of vulnerability in sulfuric acid alkylation units include contactors, reactor effluent lines, reboilers, deisobutanizer overhead systems, and the caustic treating section. ([Figure 3-62-2](#) and [Figure 3-62-3](#))
- c) Acid and acid esters can carry over from the treating section and get into the distillation section. Acid concentrates in the reboilers and boils into the overhead. Similarly, acid esters can thermally decompose in the distillation section reboilers to form sulfurous or sulfuric acid, both of which vaporize and travel to the overhead.
- d) Rivulet corrosion can occur in tanks and vessels where dilute acid refluxes down the sides of the tank or vessel. This condition can also occur at the air to liquid interface or rag layer.

- e) Hydrogen grooving can occur in low-flow or stagnant areas such as in storage tanks, rail cars, or dead-legs.
- f) Vessels handling sulfuric acid can be severely corroded when cleaning the vessel for internal inspection. Mixing concentrated sulfuric acid with cleaning water (which will also release a lot of heat and energy) will form dilute, highly corrosive acid that can cause a lot of damage in short period of time.

3.62.5 Appearance or Morphology of Damage

- a) Attack can be localized or general depending upon acid concentration, flow velocity, and the location of vapor/liquid interface areas.
 - 1. Localized corrosion can occur in piping or other areas with high flow.
 - 2. Carbon steel weld HAZs can be attacked rapidly.
 - 3. Rivulet corrosion, hydrogen grooving, and corrosion at the vapor/liquid or air/liquid interface are localized.
- b) Localized corrosion can be so uniform that VT may not notice the transition from shallow to deep metal loss.
- c) “Knife-line” grooving is typical at tops of horizontal piping where hydrogen bubbles form and travel along the top of the pipe. Areas of “fan”-shaped or “delta”-shaped corrosion are common at elbows.
- d) Sulfuric acid attacks slag left from welding.
- e) If the corrosion rate and velocity are high, there will be no scale.

3.62.6 Prevention/Mitigation

- a) Corrosion is minimized through proper materials selection and proper operation within design velocities.
- b) Alloys such as Alloy 20, Alloy 904L, and Alloy C-276 resist dilute acid corrosion and form a protective iron sulfate film on the surface.
- c) Acidified product streams can be washed with caustic to neutralize the acid.
- d) Because the cleaning of vessels containing concentrated H_2SO_4 can cause serious corrosion [see 3.62.4 f)], when carbon steel (or other non-resistant material) vessels must be emptied, a neutralization procedure that is safe and mitigates corrosion should be followed.

3.62.7 Inspection and Monitoring

- a) Localized corrosion due to sulfuric acid can be detected and measured by UT and RT.
- b) Permanently mounted thickness monitoring sensors can be used.
- c) Corrosion can be monitored with coupons and ER probes.
- d) To avoid potential corrosion from clean-out of vessels containing concentrated H_2SO_4 , they should be considered for non-intrusive inspection. When clean-out is performed, inspection should be considered after clean-out to ensure no significant damage resulted from the cleaning process.

3.62.8 Related Mechanisms

None.

3.62.9 References

1. NACE Publication 5A151, *Materials of Construction for Handling Sulfuric Acid*, NACE International, Houston, TX, 1985.
2. S.W. Dean and G.D. Grab, "Corrosion of Carbon Steel by Concentrated Sulfuric Acid," Paper No.147, *Corrosion/84*, NACE International, Houston, TX.
3. S.K. Brubaker, "Materials of Construction for Sulfuric Acid," *Process Industries Corrosion—The Theory and Practice*, NACE International, Houston, TX, pp. 243–258.
4. API Recommended Practice 581, *Risk-Based Inspection Methodology*, American Petroleum Institute, Washington, DC.
5. *Corrosion Control in the Refining Industry*, NACE Course Book, NACE International, Houston, TX, 1999.
6. NACE Standard SP0294, *Design, Fabrication, and Inspection of Storage Tank Systems for Concentrated Fresh and Process Sulfuric Acid and Oleum at Ambient Temperatures*, NACE International, Houston, TX.
7. M. Davies, "Materials Selection for Sulfuric Acid," MTI Publication No. MS-1, Materials Technology Institute of the Chemical Processes Industries, St. Louis, MO.

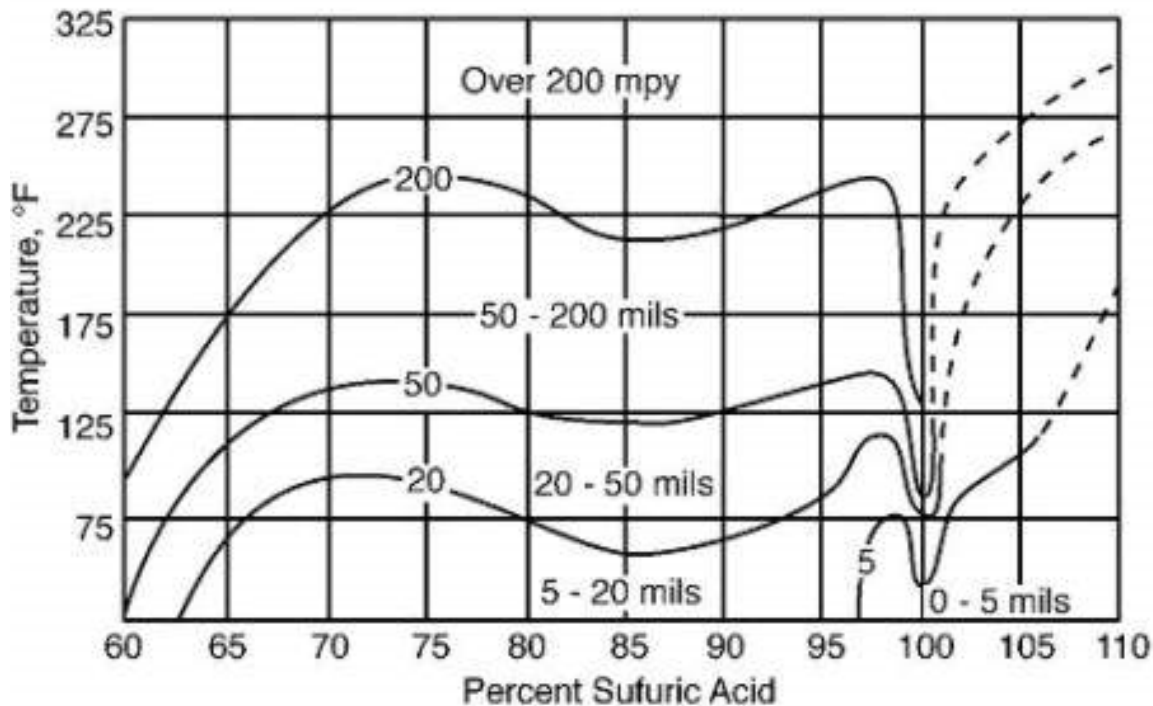


Figure 3-62-1—Sulfuric acid corrosion rate chart for carbon steel.



Figure 3-62-2—Accelerated sulfuric acid corrosion under a baffle.



Figure 3-62-3—Grooving corrosion in the carbon steel vapor line from an alkaline water wash drum in a sulfuric acid alkylation unit.

3.63 Temper Embrittlement

3.63.1 Description of Damage

Temper embrittlement is the reduction in fracture toughness due to a metallurgical change that can occur in some low-alloy steels as a result of long-term exposure in the temperature range of about 650 °F to 1070 °F (345 °C to 575 °C). This change causes an upward shift in the ductile-to-brittle transition temperature as measured by Charpy impact testing. Although the loss of toughness is not evident at operating temperature, equipment that is temper embrittled may be susceptible to brittle fracture during start-up and shutdown.

3.63.2 Affected Materials

- a) Primarily 2.25Cr-1Mo low-alloy steel, 3Cr-1Mo (to a lesser extent), and the HSLA Cr-Mo-V rotor steels.
- b) Older generation 2.25Cr-1Mo materials manufactured prior to 1972 may be particularly susceptible. Some HSLA steels are also susceptible.
- c) The C-0.5Mo, 1Cr-0.5Mo, and 1.25Cr-0.5Mo alloy steels are not as affected by temper embrittlement. However, other high-temperature damage mechanisms promote metallurgical changes that can alter the toughness or high temperature ductility of these materials. Refer to API 934-C and API 934-D for additional information.
- d) Weld materials are generally more affected than today's low-impurity base materials.

3.63.3 Critical Factors

- a) Alloy steel composition, thermal history, metal temperature, and exposure time are critical factors.
- b) Susceptibility to temper embrittlement is largely determined by the presence of the alloying elements manganese and silicon and the tramp elements phosphorus, tin, antimony, and arsenic. The strength level and heat treatment/fabrication history can also have an effect.
- c) Temper embrittlement of 2.25Cr-1Mo steels develops more quickly at 900 °F (480 °C) than in the 800 °F to 850 °F (425 °C to 440 °C) range, but the damage is more severe after long-term exposure at 850 °F (440 °C).
- d) Some embrittlement can occur during fabrication heat treatments, but most of the damage occurs over many years of service in the embrittling temperature range.
- e) This form of damage will significantly reduce the structural integrity of a component containing a crack-like flaw. An evaluation of material toughness may be required depending on the flaw type and the severity of the operating conditions (e.g. the pressure and stress state), particularly in hydrogen service.

3.63.4 Affected Units or Equipment

- a) Temper embrittlement occurs in a variety of process units after long-term exposure to temperatures above 650 °F (345 °C). It should be noted that there have been very few industry failures related directly to temper embrittlement.
- b) Equipment susceptible to temper embrittlement is most often found in hydroprocessing units, particularly reactors, hot feed/effluent exchanger components, and hot HP separators. Other units with the potential for temper embrittlement include catalytic reforming units (reactors and exchangers), FCC units (reactors), coker units, and visbreaking units.
- c) Welds in potentially susceptible equipment are often more susceptible than the base metal.

3.63.5 Appearance or Morphology of Damage

- a) Temper embrittlement is a metallurgical change that is not readily apparent but can be confirmed through (destructive) impact testing. Damage due to temper embrittlement may result in catastrophic brittle fracture.
- b) Temper embrittlement can be identified by an upward shift in the ductile-to-brittle transition temperature measured in a CVN impact test, as compared to the non-embrittled or de-embrittled material. (Figure 3-63-1) Another important characteristic of temper embrittlement is that there is no effect on the upper shelf energy.
- c) SEM fractographs of severely temper embrittled material show primarily intergranular cracking due to impurity segregation at grain boundaries.

3.63.6 Prevention/Mitigation

a) Existing materials.

1. Temper embrittlement cannot be prevented if the material contains critical levels of the embrittling impurity elements and is exposed in the embrittling temperature range.
2. To minimize the possibility of brittle fracture during start-up and shutdown, many refiners use a pressurization sequence to limit system pressure to about 25 % of the maximum design pressure for temperatures below a minimum pressurization temperature (MPT).

NOTE The MPT might not be a single temperature but rather a pressure-temperature curve that defines safe operating conditions to minimize the likelihood of brittle fracture.

3. MPTs generally range from 350 °F (170 °C) for the earliest, most highly temper embrittled steels, down to 125 °F (50 °C) or lower for newer, temper-embrittlement-resistant steels (as required to also minimize effects of HE).
4. In addition to controlling pressure and temperature during start-up and shutdown, temper embrittlement needs to be considered in order to prevent brittle fracture when hydrotesting susceptible equipment.
5. If weld repairs are required, the effects of temper embrittlement can be temporarily reversed (the metal can be de-embrittled) by heating at 1150 °F (620 °C) for 2 hr per 1 in. (25 mm) of thickness and rapidly cooling to room temperature. Re-embrittlement will occur over time if the material is re-exposed to the embrittling temperature range.

b) New materials.

1. The best way to minimize the likelihood and extent of temper embrittlement is to limit the acceptance levels of manganese, silicon, phosphorus, tin, antimony, and arsenic in the base metal and welding consumables. In addition, strength levels and PWHT procedures should be specified and carefully controlled.
2. A common way to minimize temper embrittlement is to limit the “J” factor for base metal and the “X” factor for weld metal, based on material composition as follows:

$$J = (Si + Mn) \times (P + Sn) \times 10^4 \quad \{\text{elements in wt \%}\}$$

$$X = (10P + 5Sb + 4Sn + As)/100 \quad \{\text{elements in ppm}\}$$

3. Typical J and X factors used for 2.25 Cr steel are a maximum of 100 and 15, respectively. Studies have also shown that limiting the (P + Sn) to less than 0.01 % is sufficient to minimize temper embrittlement because (Si + Mn) control the rate of embrittlement.

4. A newer and less widely used factor called the Equivalent Phosphorus content has been developed for base metal and weld metal and is defined as follows:

$$P = C + Mn + (Mo+Cr)/3 + Si/4 + 3.5 \times [(10 \times P) + (5 \times Sb) + (4 \times Sn) + As] \text{ \{elements in wt \% \}}$$

5. Expert metallurgical advice should be solicited to determine acceptable composition, toughness, and strength levels, as well as appropriate welding, fabrication, and heat treating procedures for new low-alloy steel heavy wall equipment operating in the temper embrittlement or creep range.

3.63.7 Inspection and Monitoring

- a) Inspection is not normally used to detect temper embrittlement, but awareness of susceptible equipment can help prevent future damage.
- b) A method of monitoring is to install blocks of original heats of the alloy steel material inside the reactor. Samples are periodically removed from these blocks for impact testing to establish and monitor the ductile-brittle transition temperature. The test blocks should be strategically located near the top and bottom of the reactor to make sure that the test material is exposed to both inlet and outlet conditions.
- c) Process conditions should be carefully monitored to ensure that a proper pressurization/temperature sequence is followed to help prevent brittle fracture due to temper embrittlement. This includes both start-up and shutdown and also applies to the hydrotesting of equipment.

3.63.8 Related Mechanisms

Brittle fracture (3.11).

3.63.9 References

1. R.A. Swift, "Temper Embrittlement in Low-alloy Ferritic Steels," Paper No. 125, *Corrosion/76*, NACE International, Houston, TX.
2. R.A. White and E.F. Ehmke, *Materials Selection for Refineries and Associated Facilities*, NACE International, Houston, TX, 1991, pp. 53–54.
3. R. Viswanathan, *Damage Mechanisms and Life Assessment of High-temperature Components*, ASM International, 1989.
4. API Recommended Practice 934-A, *Materials and Fabrication of 2¼Cr-1Mo, 2¼Cr-1Mo-¼V, 3Cr-1Mo, and 3Cr-1Mo-¼V Steel Heavy Wall Pressure Vessels for High-temperature, High-pressure Hydrogen Service*, American Petroleum Institute, Washington, DC.
5. API Technical Report 934-B, *Fabrication Considerations for Vanadium-Modified Cr-Mo Steel Heavy Wall Pressure Vessels*, American Petroleum Institute, Washington, DC, April 2011.
6. API Recommended Practice 934-C, *Materials and Fabrication of 1¼Cr-½Mo Steel Heavy Wall Pressure Vessels for High-pressure Hydrogen Service Operating at or Below 825 °F (441 °C)*, American Petroleum Institute, Washington, DC.
7. API Technical Report 934-D, *Technical Report on the Materials and Fabrication Issues of 1¼Cr-½Mo and 1Cr-½Mo Steel Pressure Vessels*, American Petroleum Institute, Washington, DC, First Edition, September 2010.
8. API Recommended Practice 934-E, *Recommended Practice for Materials and Fabrication of 1¼Cr-½Mo Steel Pressure Vessels for Service Above 825 °F (440 °C)*, American Petroleum Institute, Washington, DC.
9. P. Toussaint et al., "Effect of Aging and Hydrogen on Fracture Mechanics and CVN Properties of 2.25Cr-1Mo Steel Grades—Application to MPT Issues," Paper No. 09341, *Corrosion/2009*, NACE International, Houston, TX.

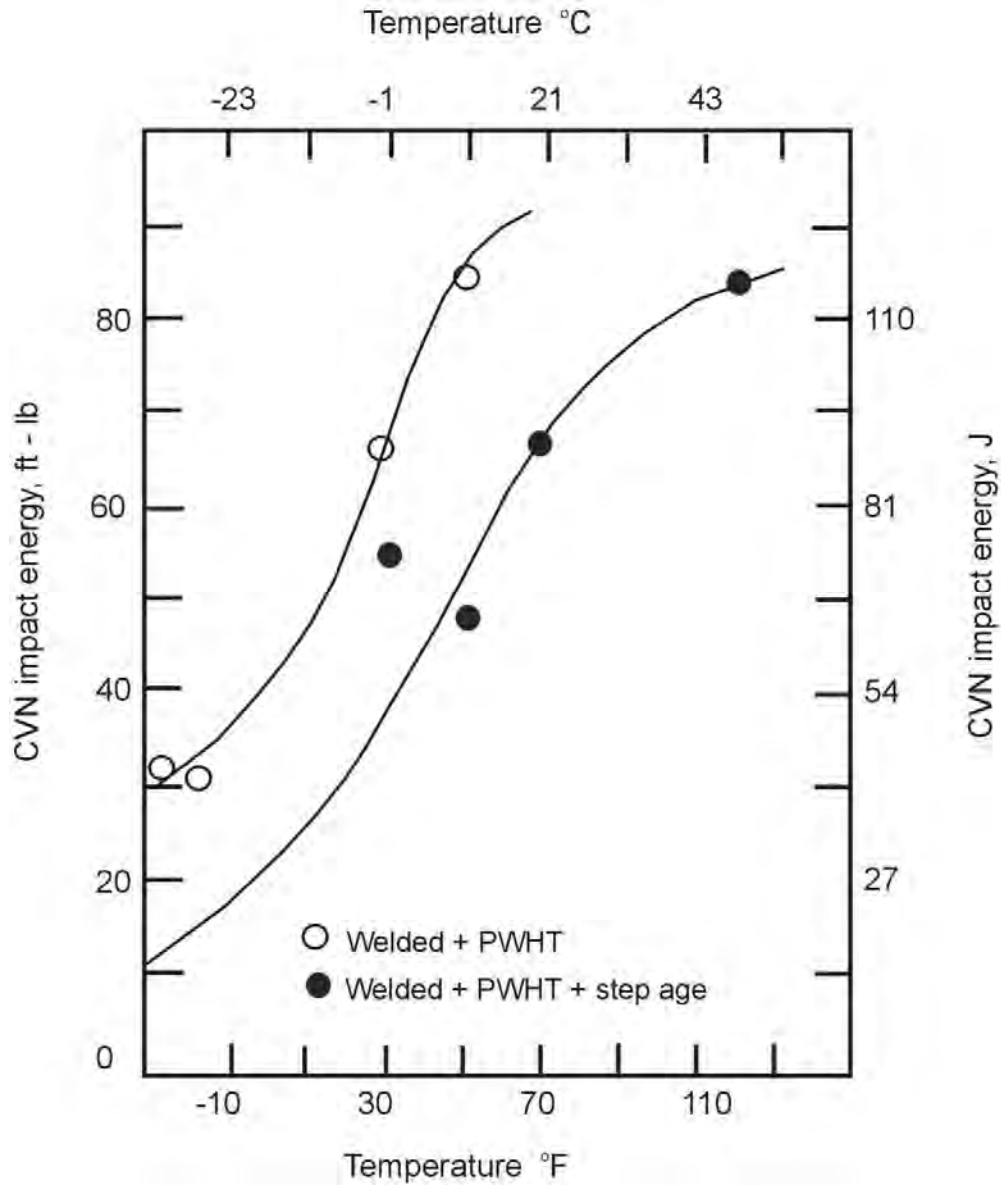


Figure 3-63-1—Plot of CVN toughness as a function of temperature showing an upward shift in the Charpy curve and the 40-ft-lb transition temperature as a result of temper embrittlement.

3.64 Thermal Fatigue

3.64.1 Description of Damage

Thermal fatigue is the result of cyclic stresses caused by variations in temperature. Damage is in the form of cracking that may occur anywhere in a metallic component where relative movement or differential expansion is constrained during repeated thermal cycling.

3.64.2 Affected Materials

All materials of construction.

3.64.3 Critical Factors

- a) Key factors affecting thermal fatigue are the magnitude of the temperature swing and the frequency [number of thermal cycles per second (or minute or day, etc.)].
- b) Time to failure is a function of the magnitude of the cyclic stress and the number of cycles, and decreases with increasing stress and increasing frequency.
- c) Since there are many variables that can affect where and whether thermal fatigue cracking will occur, it is not possible to define a specific, universal limit on allowable temperature swings. For example, rigid attachments may only require a relatively small temperature differential to promote cracking. However, as a reasonable rule of thumb, cracking may be suspected if the temperature swings exceed about 200 °F to 300 °F (110 °C to 165 °C).
- d) Damage is promoted by inflexibility to accommodate differential expansion. It is also promoted by rapid changes in surface temperature that result in a thermal gradient through the thickness or along the length of a component, e.g. from cold water impinging on a hot tube.
- e) Notches (such as the toe of a weld) and sharp corners (such as the intersection of a nozzle with a vessel shell) and other stress concentrations may serve as initiation sites.
- f) In some cases, depending on the frequency at which equipment or an entire unit is shut down and started up, start-up and shutdown can increase the susceptibility to thermal fatigue cracking.

3.64.4 Affected Units or Equipment

- a) Examples include the mix points of hot and cold streams such as hydrogen mix points in hydroprocessing units, and locations where condensate comes in contact with steam systems, such as de-superheating or attemperating equipment. (Figure 3-64-1 and Figure 3-64-2)
- b) Thermal fatigue cracking has been a major problem in coke drum shells. Thermal fatigue cracking can also occur on coke drum skirts where stresses are promoted by a variation in temperature between the drum and skirt. (Figure 3-64-3 and Figure 3-64-4)
- c) In steam-generating equipment, the most common locations are at rigid attachments between neighboring tubes in the superheater and reheater. Slip spacers designed to accommodate relative movement may become frozen and act as a rigid attachment when plugged with fly ash.
- d) Tubes in the high-temperature superheater or reheater that penetrate through the cooler waterwall tubes may crack at the header connection if the tube is not sufficiently flexible. These cracks are most common at the end where the expansion of the header relative to the waterwall will be greatest.
- e) Steam-actuated soot blowers in heaters or boilers may cause thermal fatigue damage if the first steam exiting the soot blower nozzle contains condensate. Rapid cooling of the tube by the liquid water will promote this form of damage. Similarly, water lancing or water cannon use on waterwall tubes may have the same effect.

3.64.5 Appearance or Morphology of Damage

- a) Thermal fatigue cracks usually initiate on the surface of the component, on either the ID or OD surface. They are generally wide and often filled with oxides due to elevated temperature exposure. Cracks may occur as single or multiple cracks.
- b) Thermal fatigue cracks propagate transverse to the stress, and they are usually dagger shaped, transgranular, and oxide filled. (Figure 3-64-5 and Figure 3-64-6) However, cracking may be axial or circumferential, or both, at the same location.
- c) In steam-generating equipment, cracks usually follow the toe of the fillet weld, as the change in section thickness creates a stress riser. Cracks often start at the end of an attachment lug, and if there is a bending moment as a result of the constraint, they will develop into circumferential cracks into the tube.
- d) Water in soot blowers may lead to a crazing pattern. The predominant cracks will be circumferential and the minor cracks will be axial. (Figure 3-64-7 and Figure 3-64-8)

3.64.6 Prevention/Mitigation

- a) Thermal fatigue is best prevented through design and operation to minimize fluctuating thermal stresses and thermal cycling. Several methods of prevention apply depending on the application.
 - 1. Designs that incorporate reduction of stress concentrators, blend grinding of weld profiles, and smooth transitions should be used.
 - 2. Controlled rates of heating and cooling during start-up and shutdown of equipment can lower stresses.
 - 3. Differential thermal expansion between adjoining components of dissimilar materials should be considered.
- b) Designs should incorporate sufficient flexibility to accommodate differential expansion.
 - 1. In steam-generating equipment, slip spacers should slip and rigid attachments should be avoided.
 - 2. Drain lines should be provided on soot blowers to prevent condensate in the first portion of the soot-blowing cycle.
- c) In some cases, a liner or sleeve may be installed to prevent a colder liquid from contacting the hotter pressure boundary wall.

3.64.7 Inspection and Monitoring

- a) NDE methods used to detect surface-breaking cracks using same-side inspection include:
 - 1. PT,
 - 2. MT,
 - 3. WFMT,
 - 4. ECT,
 - 5. ACFM, and
 - 6. EMAT.
- b) NDE methods used to detect surface-breaking cracks using opposite-side inspection and/or areas that are same side but not accessible include angle beam UT (SWUT or PAUT) and TOFD.

- c) AET can be used for continuous monitoring or monitoring during thermal transitions to detect mechanical energy released from cracks when strain values are elevated. Strain value elevation causing thermal fatigue cracking can occur during increase or decrease of temperatures.
- d) Temperature monitoring can be performed by installing thermocouples, where practical, on components with thick sections or that are otherwise susceptible to thermal fatigue cracking. The heating and cooling rates should be controlled to avoid steep temperature gradients.

3.64.8 Related Mechanisms

Mechanical fatigue (3.43), corrosion fatigue (3.21), and DMW cracking (3.26).

3.64.9 References

1. *Steam—Its Generation and Use*, 40th Edition, Babcock & Wilcox, 1992.
2. *Combustion: Fossil Power Systems*, Third Edition, Combustion Engineering, Windsor, CT, 1981.
3. H. Thielsch, *Defects and Failures in Pressure Vessels and Piping*, Krieger Publishing, Malabar, FL, 1977.
4. R.D. Port and H.M. Herro, *The Nalco Guide to Boiler Failure Analysis*, McGraw-Hill, New York, NY, 1991.
5. D.N. French, *Metallurgical Failures in Fossil Fired Boilers*, John Wiley and Sons, New York, NY, 1993.
6. B. Dooley and W. McNaughton, *Boiler Tube Failures: Theory and Practice*, 3 Volumes, EPRI, 1995.

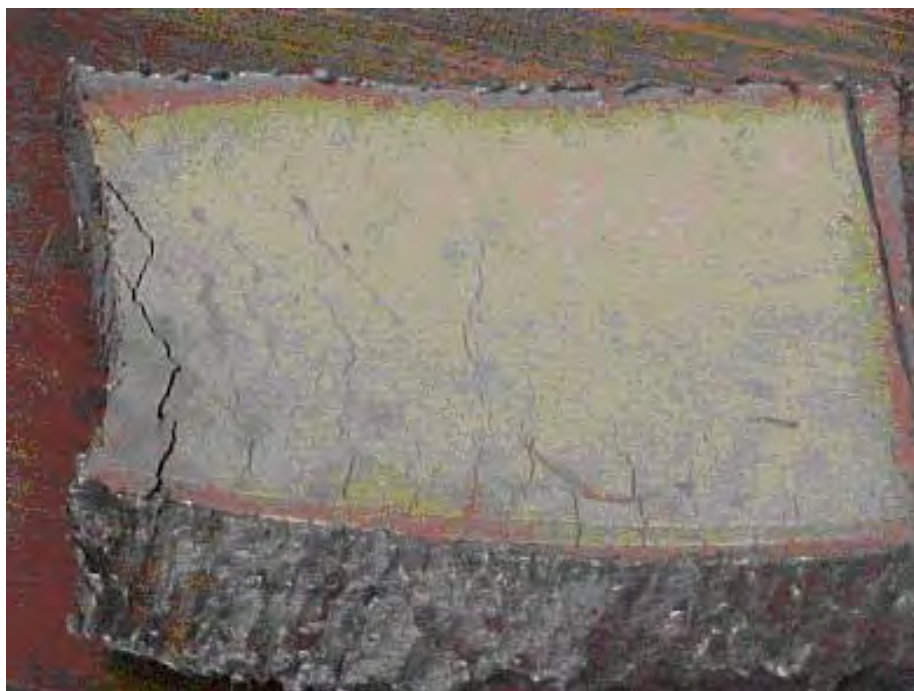


Figure 3-64-1—Thermal fatigue cracks on the inside of a heavy wall SS pipe downstream of cooler H₂ injection into a hot hydrocarbon line.

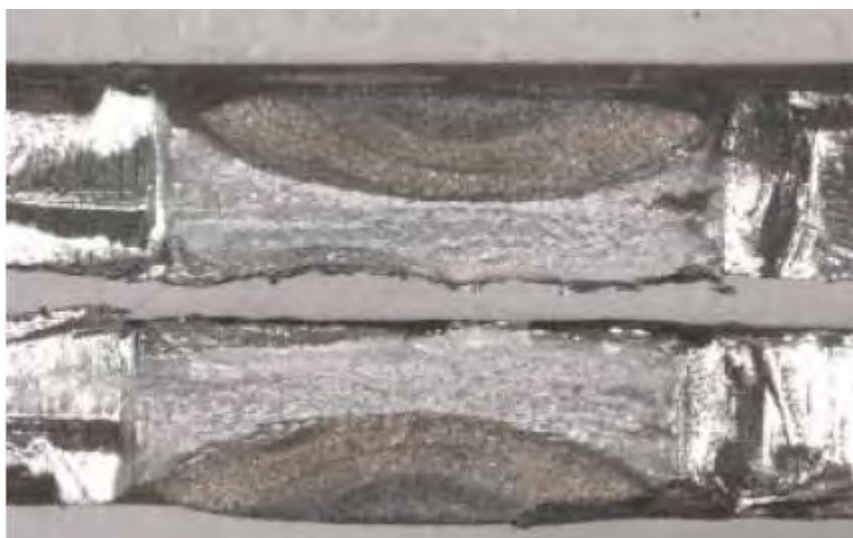


Figure 3-64-2—Thermal fatigue cracking surfaces of 304L stainless steel at a mix point in the BFW preheater bypass line around the high-temperature shift effluent exchanger in a hydrogen reformer. The delta T is 325 °F (180 °C) at an 8-in. bypass line tying into a 14-in. line. Failure occurred 3 years after start-up.

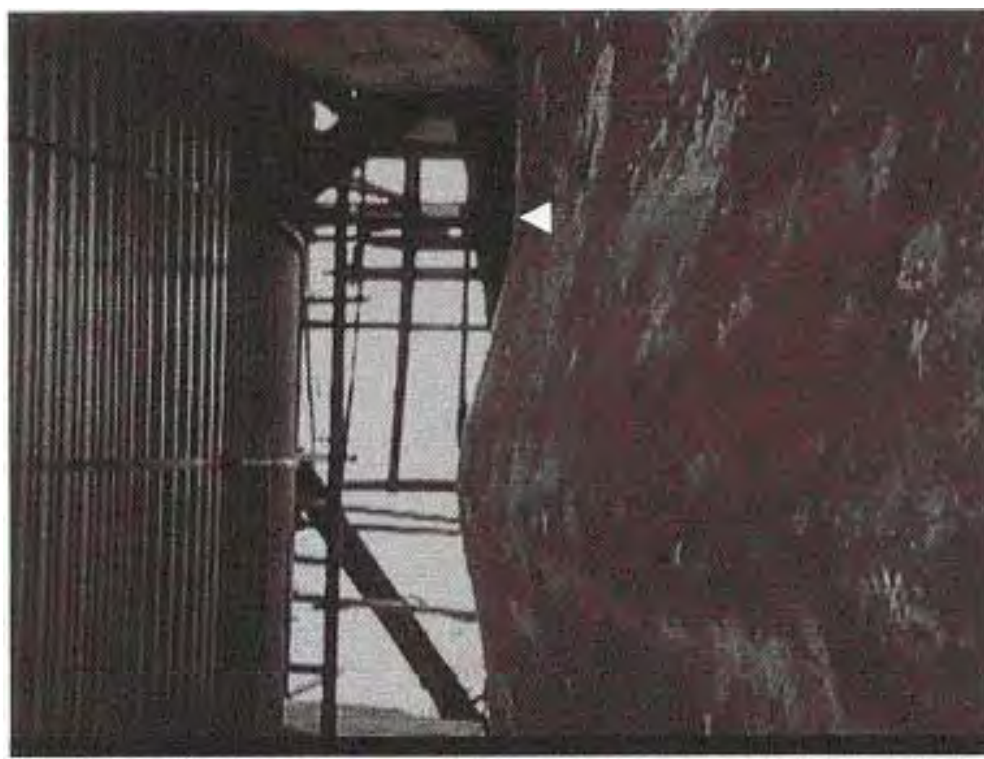


Figure 3-64-3—Bulging in a skirt of a coke drum due to thermal cycling from coker operation.



Figure 3-64-4—Thermal fatigue cracking associated with bulged skirt shown in Figure 3-64-3.

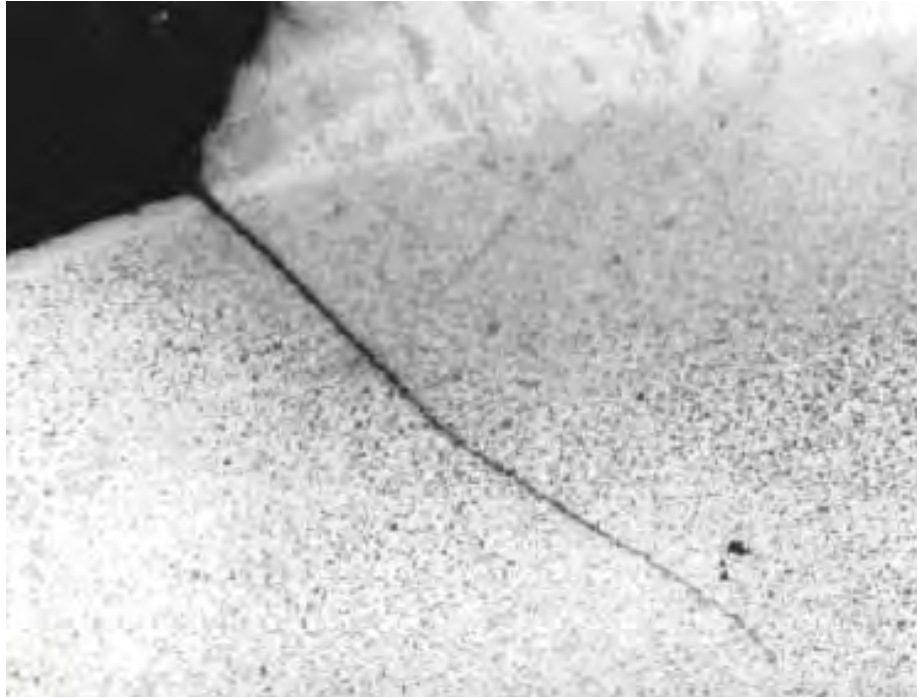


Figure 3-64-5—Metallographic section through a thermal fatigue crack in a carbon steel sample indicates origin at the toe of an attachment weld. Magnification 50X, etched.

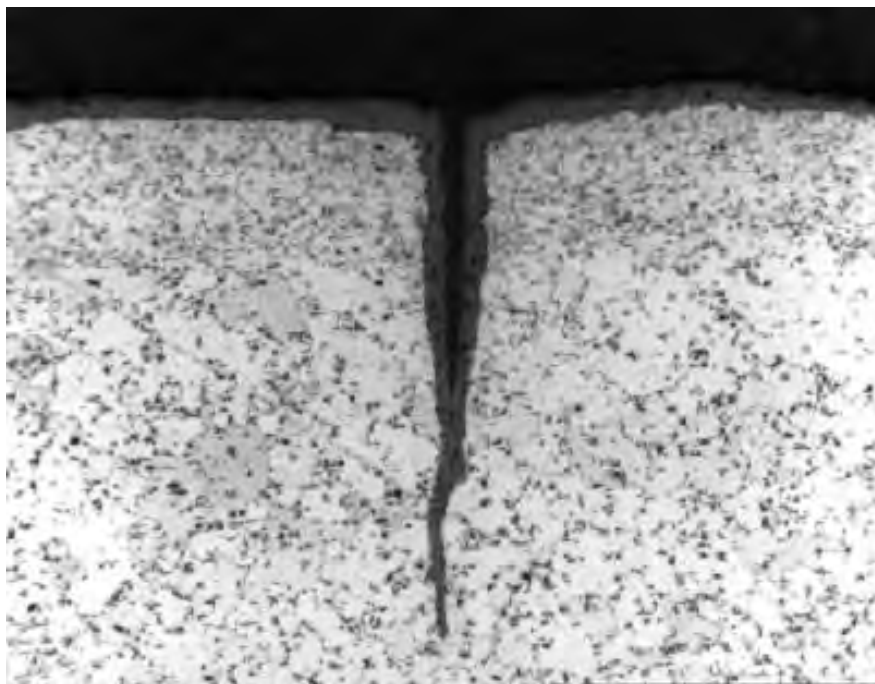


Figure 3-64-6—Cracks that develop over time will typically fill with oxide, may stop and restart (note jog part way along the crack), and do not necessarily require a change in section thickness to initiate the crack. Magnification 100X, etched.

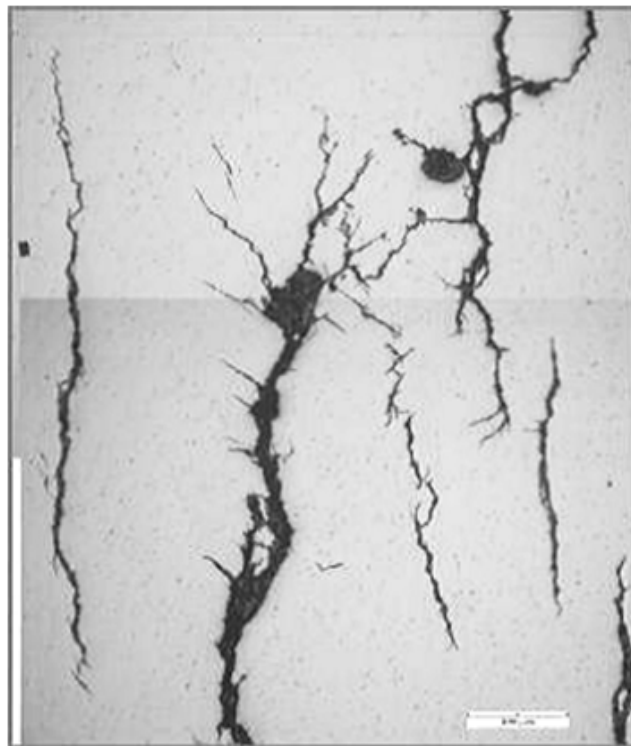


Figure 3-64-7—Metallographic cross section of a superheated steam outlet line that failed from thermal fatigue. Unetched.

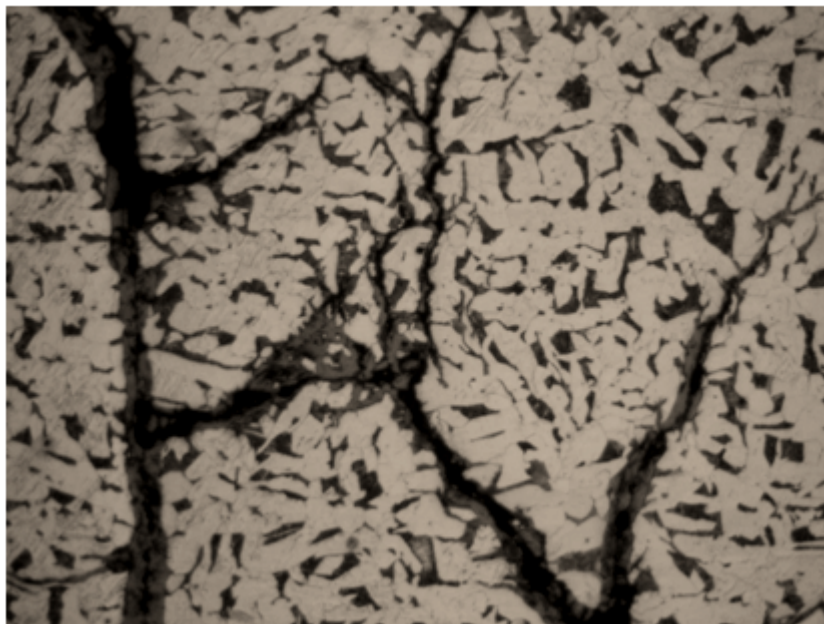


Figure 3-64-8—Photomicrograph of the same failed superheated steam outlet line shown in Figure 3-64-7. Etched.

3.65 Thermal Shock

3.65.1 Description of Damage

Thermal shock cracking can occur when high and non-uniform thermal stresses develop in a single event over a short time in a piece of equipment due to differential expansion or contraction. If the thermal expansion/contraction is restrained, stresses above the yield strength of the material can result. Thermal shock cracking usually occurs when a much colder liquid contacts a much warmer metal surface. In refining, the concern generally arises after a large equipment fire is extinguished using fire water.

3.65.2 Affected Materials

All metals and alloys.

3.65.3 Critical Factors

- a) The magnitude of the temperature differential and the coefficient of thermal expansion of the material determine the magnitude of the stress.
- b) Stainless steels have higher coefficients of thermal expansion than carbon and alloy steels or nickel-based alloys and are more likely to see higher stresses.
- c) High-temperature exposure during a fire followed by water quench to extinguish the fire can result in thermal shock cracking.
- d) Large and rapid temperature changes that can result from water quenching as a result of rain deluges could cause thermal shock cracking.
- e) Fracture is related to constraint on a component that prevents the component from expanding or contracting with a change in temperature. The metal surrounding a locally quenched area of the metal can provide the necessary constraint.
- f) Cracking in cast components such as valves may initiate at casting flaws and progress through the thickness.
- g) It is more prevalent in thick sections that can develop high thermal gradients.

3.65.4 Affected Units or Equipment

- a) FCC, coker, catalytic reforming, and high-severity hydroprocessing units are high-temperature units where thermal shock is possible.
- b) High-temperature piping and equipment in any unit can be affected.
- c) Heavy wall machinery, typically made of thick castings, can be affected, particularly those made of high-chromium steels such as 12Cr.
- d) Materials that have lost ductility, such as Cr-Mo equipment (due to temper embrittlement), are particularly susceptible to thermal shock.
- e) Equipment subjected to accelerated cooling procedures to minimize shutdown time is potentially subject to thermal shock cracking.

3.65.5 Appearance or Morphology of Damage

Surface initiating cracks may also appear as “craze” cracks.

3.65.6 Prevention/Mitigation

- a) Minimize situations where rain or fire-water deluge can contact hot equipment.

- b) Design to minimize severe restraint in hot equipment that can potentially get severely quenched.
- c) Install thermal sleeves or other protective measures to prevent inadvertent cold liquid impingement on hot pressure boundary components.

3.65.7 Inspection and Monitoring

- a) This type of damage is uncommon, but when it occurs it results in highly localized cracking that may be difficult to locate. Since it mostly occurs as a single, unpredictable event, e.g. a fire, severe storm, or major excursion or upset, it is not amenable to regular inspection monitoring. Methods to detect cracking resulting from thermal shock include:
 - 1. VT (may reveal cracking, but it might be difficult to differentiate actual cracks in the metal from superficial craze cracks in the oxide layer);
 - 2. PT;
 - 3. MT; and
 - 4. UT.

3.65.8 Related Mechanisms

Thermal fatigue ([3.64](#)) and short-term overheating—stress rupture ([3.55](#)).

3.65.9 References

- 1. *ASM Handbook—Failure Analysis and Prevention*, Volume 11, ASM International, Materials Park, OH.
- 2. API 579-1/ASME FFS-1, *Fitness-For-Service*, American Petroleum Institute, Washington, DC.

3.66 Titanium Hydriding

3.66.1 Description of Damage

Hydriding of titanium is a metallurgical phenomenon in which hydrogen diffuses into the titanium and reacts to form an embrittling hydride phase. This can result in a complete loss of ductility and fracture toughness, potentially enabling a brittle fracture, with no noticeable sign of corrosion or loss in thickness.

3.66.2 Affected Materials

Titanium and titanium alloys.

3.66.3 Critical Factors

- a) The critical factors are metal temperature, solution chemistry, and alloy composition.
- b) This is a phenomenon that occurs in specific environments at temperatures above 165 °F (75 °C) and at a pH below 3, pH above 8, or neutral pH with high H₂S content.
- c) Galvanic contact between titanium and more active materials such as carbon steel and 300 series SS promotes damage. However, hydriding can occur in the absence of a galvanic couple.
- d) Embrittlement occurs over a period of time as hydrogen is absorbed by the component and reacts to form an embrittling hydride phase. The depth and extent of hydriding will continue to increase until a complete loss of ductility results.
- e) Hydriding has also occurred in some environments as a result of the corrosion of steel that was accidentally embedded into the surface of the titanium during fabrication.
- f) Iron sulfide scale formed from the corrosion of steel in upstream units and equipment can be carried into titanium equipment and cause hydrogen pickup and resulting hydriding.
- g) The solubility of hydrogen in pure titanium and alpha-beta titanium alloys (e.g. Gr. 2, Gr. 7, Gr 12, and Gr. 16) is limited to 50 ppm to 300 ppm. When the hydrogen concentration exceeds this solubility limit, hydride is formed. Beta alloys are more tolerant of hydrogen, and 2000 ppm can be absorbed without causing detrimental hydriding. However, beta alloys are not typically used for refinery process equipment.

3.66.4 Affected Units or Equipment

- a) Titanium has mainly been used in heat exchangers and air coolers, primarily to take advantage of the corrosion resistance of titanium tubes in these services. Damage has occurred primarily in SWSs and amine units in the overhead condensers or air coolers and other heat exchanger tubes, as well as some piping and other titanium equipment operating above about 165 °F (75 °C). In most cases, cracking has occurred during maintenance operations, e.g. turnarounds, rather than while the equipment was in service.
- b) Hydriding can also occur in hydrogen atmospheres at temperatures > 350 °F (175 °C), especially in the absence of moisture or oxygen.
- c) Cathodic protection potentials less -0.9 v SCE on titanium equipment can promote hydrogen entry and hydriding.

3.66.5 Appearance or Morphology of Damage

- a) Titanium hydriding is a metallurgical change that is not visually apparent and can only be confirmed through metallurgical examination ([Figure 3-66-2](#) and [Figure 3-66-3](#)) or mechanical testing.

- b) The detrimental result of titanium hydriding is cracking, which will be visually apparent. (Figure 3-66-1)
 - 1. When leaks or cracking in titanium pressure retaining parts occur, titanium hydriding is likely to be anticipated as the cause, and the leaks will likely be obvious.
- c) Heat exchanger tubes that have become embrittled may remain intact until disturbed by removal of the bundle for inspection. The tubes crack as the bundle flexes when it is removed.
- d) Cracking can occur if there is an attempt to re-roll tube ends that have become embrittled.
- e) Another possible ramification that has occurred is ignition and burning of titanium tubes.
 - 1. Titanium is a reactive metal that can combust in the presence of heat and oxygen. Caution should be exercised when exposing titanium to heat or flame during downtimes. Exposure to pyrophoric materials or cutting torches has resulted in metal fires.

3.66.6 Prevention/Mitigation

- a) The risk of failure due to titanium hydriding should be considered in known hydriding services such as amine or SWS overhead condensers.
- b) Precautions should be taken during outages to avoid brittle fracture of titanium components, e.g. air cooler tubes, when used in known hydriding services.
- c) Where galvanic contact has promoted hydriding, the problem can be avoided by using all titanium construction or by electrically isolating the titanium from non-titanium components. Eliminating the galvanic couple may not prevent hydriding in alkaline SW environments.

3.66.7 Inspection and Monitoring

- a) Cracks resulting from titanium hydriding are typically found through VT.
- b) Sampling and destructive testing using microstructural analysis and/or mechanical testing methods are typically required to confirm the presence and degree of hydriding.
- c) NDE techniques are generally not employed in refining to detect hydriding. Rather, sampling and destructive testing are used when there is a need to determine whether hydriding has occurred.
- d) Embrittlement can be confirmed by a bend, crush, or impact (hammer) test in a vice. Unaffected titanium will be crushed or bent in a ductile fashion while embrittled components will crack or shatter (sometimes like glass) with little or no sign of ductility.
- e) ECT techniques have been used in other industries, e.g. in the power and aircraft industries, to detect both the presence of hydriding as well as cracks within the hydrided layer of components. Because of the effect on eddy current response of the change in electrical resistivity caused by hydriding, hydriding may appear as, and be misinterpreted as, wall thinning.
 - 1. With no track record of use in oil refinery equipment, such techniques should be used with caution, including validation of the technology and methodology.

3.66.8 Related Mechanisms

Hydriding is a damage mechanism that is unique to a few materials including alloys of titanium and zirconium. However, it is considered a form of HE (3.40) and could result in a brittle fracture (3.11).

3.66.9 References

1. B.E. Hopkinson and O. Fermin Hernandez, "Use of Titanium in Petroleum Refining," *Materials Performance*, September 1990, pp. 48–52.
2. J.B. Cotton, "Using Titanium in the Chemical Plant," *Chemical Engineering Progress*, Vol. 66, No. 10, 1970, p. 57.
3. L.C. Covington, "Factors Affecting the Hydrogen Embrittlement of Titanium," Paper No. 75, *Corrosion/75*, NACE International, Houston, TX.
4. L.C. Covington, "The Influence of Surface Condition and Environment on the Hydriding of Titanium," *Corrosion*, Vol. 35, No. 8, 1979, pp. 378–382.
5. I. Phillips, P. Pool, and L.L. Shreir, "Hydride Formation During Cathodic Polarization of Ti," and "Effect of Temperature and pH of Solution on Hydride Growth," *Corrosion Science*, Vol. 14, 1974, pp. 533–542.
6. L.A. Charlot and R.H. Westerman, "Low Temperature Hydriding of Zircaloy-2 and Titanium in Aqueous Solutions," *Electrochemical Technology*, Vol. 6, 1968.
7. R.W. Schutz, J.S. Grauman, and C. Covington, "Determination of Cathodic Protection Limits for Prevention of Titanium Tube Hydride Embrittlement in Salt Water," Paper No. 110, *Corrosion/89*, NACE International, Houston, TX.
8. Z.F. Wang, C.L. Briant, and K.S. Kumar, "Electrochemical, Galvanic and Mechanical Responses of Grade 2 Titanium in 6% Sodium Chloride Solution," *Corrosion*, Vol. 55, No. 2, 1999, pp. 128–138.
9. D.J. Schumerth and T. Demers, "Hydrogen Embrittlement in Titanium Steam Surface Condenser Tubing Truths, Myths & Misnomers," :
https://cdn.ymaws.com/titanium.org/resource/resmgr/2010_2014_papers/SchumerthDennisTiUSA2013Indu.pdf.
10. D.J. Hagemaijer, "Nondestructive Detection of Hydrides and Alpha-Case in Titanium Alloys," *Titanium Science and Technology*, R.I. Jafee and H.M. Burte, Eds., 1972, pp. 755–765.
11. MTI Communications, Summer 2012, "Project Update: Developing a Commercially Available NDE Method for Detecting Titanium Hydriding," Materials Technology Institute, St. Louis. MO.



Figure 3-66-1—Titanium heat exchanger tube that failed from hydriding in a SW cooler. The cooling medium was seawater.



Figure 3-66-2—High-magnification photomicrograph of a cross section of the tube shown in Figure 3-66-1 through the crack tip. Magnification 200X.



Figure 3-66-3—Another high-magnification photomicrograph of a cross section of the tube in Figure 3-66-1, showing more of the cross section through the tip of the crack. Titanium hydrides are more clearly discernable. Magnification 400X.

3.67 Wet H₂S Damage (Blistering/HIC/SOHIC/SSC)

3.67.1 Description of Damage

This section describes four types of damage that result in blistering and/or cracking of carbon steel, one of which also affects low-alloy steels and some other high-strength or hardenable materials, in wet H₂S environments.

a) Hydrogen Blistering

Hydrogen blisters form bulges primarily on the ID surface of pressure vessels. Hydrogen blistering is rare in seamless pipe but can occur in seam-welded pipe. Blisters are caused by the hydrogen atoms that form on the surface of the steel as a result of corrosion reactions. Sulfur acts as a *recombination poison*, delaying the combining of hydrogen atoms into hydrogen gas molecules (H₂), allowing the hydrogen atoms to linger on the steel surface. The small hydrogen atoms can then readily diffuse into the steel. (This *hydrogen charging* effect applies to all types of wet H₂S damage.) The hydrogen atoms diffusing into the steel collect at discontinuities such as inclusions or laminations, where they then combine to form H₂ gas, because there is no recombination poison within the steel to inhibit the reaction. The hydrogen gas molecules thus become trapped at the site because they are too large to diffuse away through the steel. As corrosion proceeds, hydrogen atoms continue to form on the surface and then diffuse into the steel to become trapped as H₂ at the collection sites, building the H₂ gas pressure to the point where local deformation occurs, forming a blister. Blistering only results from hydrogen generated by corrosion, not from hydrogen gas in the process stream. (See [Figure 3-67-1](#) and [Figure 3-67-2](#) for blistering damage.)

HCN accentuates the problem by weakening protective films on the metal surface, thereby increasing the rate of corrosion. This in turn leads to increased hydrogen charging and associated wet H₂S damage. (This also applies to all types of wet H₂S damage.)

b) Hydrogen-induced Cracking (HIC)

HIC results from the same cause as blistering, i.e. from hydrogen atoms diffusing into the steel as a result of corrosion. However, in this case, when the hydrogen atoms diffuse into the steel, rather than forming blisters, internal separations parallel to the surface of the steel result. Again, it is the pressure buildup resulting from hydrogen atoms combining to form H₂ gas that cause the internal separations within the wall of the vessel. The separations are initially microscopic in size but can connect together to form macroscopic-sized cracks, by growing into one large separation on the same plane parallel to the surface or more commonly by linking up with HIC on different planes (at different depths into the wall), eventually forming a thru-wall leak path. Interconnecting cracks between HIC separations on different planes have a stair step appearance, and so HIC is sometimes referred to as “stepwise cracking.” (See [Figure 3-67-3](#) to [Figure 3-67-5](#) for HIC damage.)

c) Stress-oriented Hydrogen-induced Cracking (SOHIC)

SOHIC results from an array of HIC (separations or cracks) stacked on top of each other. When acted upon by a high stress level (residual or applied), the stacked HIC will connect and create a thru-thickness crack that is perpendicular to the surface. SOHIC most often occurs in the base metal adjacent to weld HAZs, the residual stress from welding being the most common driver of SOHIC. SOHIC can initiate from the stacked HIC alone, from sulfide stress cracks, or from other crack-like defects or stress concentrations. SOHIC is a potentially more damaging form of cracking than HIC because of its relatively higher rate of developing a thru-wall crack. In addition, an absence of visual blistering may leave a false sense of security that H₂S damage is not active, yet subsurface SOHIC may be present. (See [Figure 3-67-6](#) to [Figure 3-67-8](#) for SOHIC damage.)

d) Sulfide Stress Cracking (SSC)

SSC is the cracking of a susceptible metal under the combined action of tensile stress and corrosion in the presence of water and H₂S. SSC is a form of HE cracking (see [3.40](#)) resulting from absorption of atomic hydrogen that is produced on the metal surface by the corrosion process. In addition to carbon steel and low-alloy steels, martensitic stainless steels such as Type 410 are also susceptible if hardness is not controlled to a low enough level.

SSC occurs in high-strength (high-hardness) steels but can also initiate in highly localized zones of high hardness in weld metal and HAZs. While SSC is uncommon in modern (post-1980) steels, zones of high hardness can sometimes be found in weld cover passes and attachment welds that are not tempered (softened) by subsequent passes. PWHT is beneficial in reducing the high hardness and residual stresses that render steel susceptible to SSC and is essential when welding hardenable low-alloy steels including Cr-Mo steels, as well as martensitic stainless steels. Some carbon steels contain REs that form hard areas in the HAZ that will not temper at normal stress-relieving temperatures. Using preheat helps minimize these hardness problems. While high-strength steels are susceptible to SSC, they are only used in limited applications such as valve internals and similar internal components in the refining industry.

Hard welds and hard spots within otherwise soft welds can arise with SAW when an active flux is used along with high welding voltage. This high hardness can lead to SSC. (See Reference 9.)

The time to failure by SSC decreases as the steel strength, level of tensile stress, and hydrogen charging potential of the environment increase. (See [Figure 3-67-9](#) and [Figure 3-67-10](#) for SSC damage.)

3.67.2 Affected Materials

Carbon steel, and in the case of SSC, low-alloy steels, and martensitic stainless steels.

3.67.3 Critical Factors

- a) A liquid water phase containing H_2S , i.e. a *sour environment*, must be present and must contact the steel in order for wet H_2S damage to occur. (Equipment highly susceptible to SSC can fail even during short SW excursions such as might be encountered during equipment shutdowns.) Beyond this, the critical factors that affect and differentiate the various forms of wet H_2S damage are environmental conditions (H_2S level, pH, contaminants, and temperature), material properties [microstructure and hardness (which correlates to strength)], and tensile stress level (applied or residual).
- b) All of these damage mechanisms are related to the absorption and permeation of hydrogen in steels.
- c) H_2S level.
 1. Hydrogen permeation increases with increasing H_2S partial pressure due to a concurrent increase in the H_2S concentration in the water phase.
 2. A value of 50 ppmw H_2S in the water phase is often stated as the minimum concentration where wet H_2S damage can occur. However, there are cases where cracking has occurred at lower concentrations or during upset conditions where wet H_2S was not ordinarily anticipated. The presence of as little as 1 ppmw of H_2S in the water has been found to be sufficient to cause hydrogen charging of the steel.
 3. Susceptibility to SSC increases with increasing H_2S partial pressure in the gas phase, as long as there is a water phase present concurrently. An H_2S partial pressure above about 0.05 psia (0.0003 Mpa) can cause SSC in steels with a tensile strength above about 90 ksi (620 MPa), in steels with localized zones of weld or weld HAZ hardness above 237 HB, or in non-PWHT'd or inadequately PWHT'd Cr-Mo steel welds. This partial pressure value is based primarily on oilfield experience and is not exact. The H_2S partial pressure to cause SSC will vary depending on other contributing factors, including steel strength and hardness, pH, and stress level.
- d) pH.
 1. Hydrogen permeation and diffusion rates in steel have been found to be minimal at pH 7 and increase at both higher and lower pH.
 2. Decreasing pH below 7 increases the potential for wet H_2S damage. At pH < 4, only a small amount (ppm levels) of H_2S is needed. However, wet H_2S damage can also occur at pH above 7. If an environment with an alkaline pH is corrosive and contains H_2S , e.g. ammonium bisulfide, wet H_2S damage can still occur.

3. Increasing levels of ammonia may push the pH higher into the range where cracking can occur.
4. Rich amine solutions are also an alkaline environment where wet H₂S damage can occur. See 3.3.

e) Contaminants.

1. Salts or other species in the water phase that decrease the pH or increase the corrosion rate will increase the hydrogen charging rate and, therefore, the severity of the wet H₂S damage environment.
2. HCN in the water phase can cause increased corrosion rates, which significantly increases hydrogen permeation in alkaline (high-pH) SW and thereby increases the potential for all forms of wet H₂S damage. For example, at pH > 7.6 with 20 ppmw dissolved HCN in the water, as little as 1 ppmw total sulfide content in the water can cause SSC.

f) Temperature.

1. Blistering, HIC, and SOHIC have been found to occur between ambient temperature and 300 °F (150 °C) or higher.
2. SSC potential is greatest at about 70 °F (20 °C) and decreases with increasing or decreasing temperature. This is likely related to the rate of diffusion of hydrogen and its behavior in steel at different temperatures. SSC is generally a concern below about 200 °F (95 °C); however, the limiting temperature above which SSC is no longer a concern will depend on the situation, i.e. on the hardness of the steel involved and the severity of other environmental factors such as pH.
 - If susceptible metals become charged with hydrogen during high-temperature exposure [e.g. above 200 °F (95 °C)], they can subsequently crack when cooled back down to ambient.

g) Microstructure.

1. Blistering and HIC are strongly affected by the presence of inclusions and laminations, which provide sites for diffusing hydrogen to accumulate.
 - Flat, elongated manganese sulfide (MnS) inclusions produced by ordinary steel plate rolling practices are particularly detrimental. However, steel chemical composition and manufacturing methods can be tailored to produce HIC-resistant steels. (See Reference 6.)
 - Improving steel cleanliness and processing to minimize blistering and HIC damage may still leave the steel susceptible to SOHIC.
2. HIC is often found in so-called “dirty” steels with high levels of inclusions or other internal discontinuities from the steel-making process.

h) Hardness.

1. Hardness is primarily an issue with SSC. Blistering, HIC, and SOHIC damage are not related to steel hardness. Typical carbon steels used in refinery applications are not expected to be susceptible to SSC because their strength and hardness is sufficiently low. Welds in carbon steel should be controlled to produce weld hardness < 200 HB, and they will typically achieve this without any special precautions. Carbon steel welds are not susceptible to SSC unless localized zones of hardness above 237 HB are present.
 - The welds in submerged-arc-welded steel pipe where an acid flux and high welding voltage were used can have hard zones sufficiently hard to cause SSC.
2. High-strength steels (generally those with hardness greater than 22 HRC) or steels that can be hardened by welding, such as Cr-Mo steels, can be susceptible to SSC, and steps need to be taken, such as limiting the hardness of the material or applying PWHT to reduce the hardness of the welds, to prevent SSC. (See Reference 8.)

i) Tensile stress level.

1. Blistering and HIC damage develop without applied or residual stress. PWHT will not prevent them from occurring.
2. The tensile stress needed to cause SOHIC typically comes from weld residual stresses, which, in the absence of thermal stress relief, are typically very high, i.e. approaching the yield strength. High local stresses or notch-like discontinuities such as shallow sulfide stress cracks can serve as initiation sites for SOHIC. PWHT is somewhat effective in preventing or reducing SOHIC damage.
3. The tensile stress needed to cause SSC in a susceptible material can come from applied stress or residual stress.
 - High-strength components are typically used in the non-welded condition and, therefore, are most likely to fail from applied stress. A highly susceptible material, e.g. one with very high hardness, needs relatively little tensile stress to cause SSC.
 - Hardenable steels that are welded need to be PWHT'd to reduce hardness in order to avoid SSC, and the PWHT will also relieve residual stresses. PWHT (for stress relief) of carbon steel is normally not necessary, but if there is concern for localized hard spots in the HAZ due to the chemical composition of the steel, PWHT will relieve the weld residual stresses even if it does not reduce the hardness of the hard spots, and relief of the residual stresses will help minimize the likelihood of SSC.

3.67.4 Affected Units or Equipment

- a) Blistering, HIC, SOHIC, and SSC damage can occur throughout the refinery wherever there is a wet H₂S environment present.
- b) In hydroprocessing units, an ammonium bisulfide concentration above 2 % increases the potential for blistering, HIC, and SOHIC.
- c) Cyanides, particularly in the vapor recovery sections of FCC and delayed coking units, significantly increase the probability and severity of blistering, HIC, and SOHIC damage. Typical locations include fractionator overhead drums, fractionation towers, absorber and stripper towers, compressor interstage separators and knockout drums, and various heat exchangers, condensers, and coolers.
- d) SWS and amine regenerator overhead systems are especially prone to wet H₂S damage because of generally high ammonia or ammonium bisulfide concentrations and cyanides.
- e) SSC is most likely found in hard welds and HAZs and in high-strength components including bolts, relief-valve springs, 400 series SS valve trim, and compressor shafts, sleeves, and springs.

3.67.5 Appearance or Morphology of Damage

- a) All four forms of wet H₂S damage are best illustrated though the photos and diagrams shown in [Figure 3-67-1](#) to [Figure 3-67-10](#).
- b) Hydrogen blisters appear as bulges, most often on the ID surface of the steel, but can be found anywhere in the shell plate or head of a pressure vessel. Blistering has been found on rare occasions in seamless pipe; however, large-diameter seam-welded pipe, which is typically made from plate, similar to a pressure vessel, will have susceptibility comparable to pressure vessels. Blistering has even been seen in the middle of a weld, but this is very rare.
- c) Late-stage HIC or SOHIC will create surface-breaking cracks.
- d) In pressure-containing equipment, SOHIC and SSC damage are most often associated with weldments.

- e) Blisters and HIC typically are not associated with welds but rather occur within and sometimes throughout a shell plate or course. However, they can grow toward and intersect a weld, which increases the likelihood for SOHIC in the HAZ and development of a thru-wall crack.

3.67.6 Prevention/Mitigation

- a) Effective barriers, including alloy cladding and coatings, that separate the surface of the steel from the wet H₂S environment can prevent blistering, HIC, and SOHIC. Barrier coatings can also prevent SSC of the underlying material, but they are often considered a temporary measure until a more permanent solution can be put in place.
- b) Process changes that affect the pH of the water phase and/or ammonia or cyanide concentration can help to reduce blistering, HIC, and SOHIC. A common practice is to utilize wash water injection to dilute the HCN concentration, e.g. in FCC gas plants. Cyanides can be converted to harmless thiocyanates by injecting dilute streams of ammonium polysulfides. Injection facilities require careful design.
- c) HIC-resistant steels can be used to minimize the susceptibility to blistering and HIC damage. Detailed materials and fabrication guidance can be found in Reference 6.
- d) PWHT can help minimize susceptibility to SOHIC.
- e) PWHT will not prevent blistering or HIC, because they are not initiated by stress and usually occur away from and not associated with welds.
- f) SSC in welds can generally be prevented by limiting the hardness of carbon steel welds and HAZs to 200 HB maximum. Similar, but slightly higher, maximum hardness limits are normally applied to Cr-Mo steels for which high hardness is prevented by using preheat, PWHT, and welding procedure control.
- g) High-strength materials should be selected in accordance with NACE MR0103/ISO 17945.
- h) Specialized corrosion inhibitors can be used.

3.67.7 Inspection and Monitoring

- a) Process conditions should be monitored and evaluated by process engineers and corrosion or materials specialists to identify equipment where conditions are most likely to promote wet H₂S damage. Field sampling of the free water phase should be performed on a periodic or as-needed basis to monitor conditions or changes in conditions, particularly if water washing or polysulfide injection is used.
 - b) Inspection for blistering is normally done by internal VT.
 - c) Inspection for SOHIC typically focuses on weld seams and nozzles. For details of inspection plans including methods, coverage, and surface preparation, as well as repair, see Reference 1.
 - d) Cracks from SOHIC or surface-breaking HIC may be seen visually. However, to enable crack detection at an early stage, WFMT, ECT, or ACFM techniques can be used. Surface preparation by grit blasting, high-pressure water blasting, flapper wheel cleaning, or other method is usually required for WFMT but not for ACFM or ECT. PT cannot find tight cracks and is not reliable for finding SOHIC or HIC.
1. It has become increasingly common to inspect welds on new pressure vessels intended for sour service using WFMT or another high-resolution NDE method. This is done to ensure there are no remaining flaws associated with the welds that would not have been found using standard fabrication inspection protocols when the vessel is first put into service. However, this was not done for most vessels currently in service in refineries. Because of this, extensive inspection on in-service equipment, when similar, high-resolution inspection has not been performed in the past, often leads to finding small, non-growing flaws that likely have been present since initial fabrication and are likely not H₂S damage. Therefore, caution and careful assessment need to be applied.

2. SOHIC occurs in the base metal alongside the weld. If the NDE applied for wet H₂S inspection of welds, i.e. for SOHIC, finds indications in the weld metal, they are likely fabrication weld flaws rather than SOHIC.
- e) Angle beam UT techniques including external SWUT and PAUT can be used. These techniques are especially useful for volumetric inspection and crack sizing.
- f) Electric resistance instruments are not effective for measuring crack depth.
- g) Internal HIC can appear to be deep, clearly defined, individual, sharp-cornered pits when using straight beam UT for thickness measurements on vessel shells or heads. This is caused by the reflection of the ultrasonic sound wave off the internal separation. Practitioners need to be aware of this when interpreting thickness readings on equipment in wet sour service in order to not misinterpret internal HIC as ID pitting.
- h) AET can be used to locate cracks and monitor crack growth.
- i) If cracking or failure due to SSC is not visually apparent, the cracks can normally be found using MT if they are surface breaking and there is access to the surface, or angle beam UT (SWUT or PAUT) if they are subsurface or on an inaccessible internal surface.

3.67.8 Related Mechanisms

HE (3.40), hydrogen stress cracking in HF acid (3.41), and DMW cracking (3.26). Amine cracking (3.3) and carbonate cracking (3.12) can also occur in wet H₂S environments and may be similar in appearance. They are sometimes confused with wet H₂S damage.

3.67.9 References

1. NACE Standard SP0296, Detection, Repair, and Mitigation of Cracking in Refinery Equipment in Wet H₂S Environments, NACE International, Houston, TX.
2. "Fitness-For-Service Evaluation Procedures for Operating Pressure Vessels, Tanks, and Piping in Refinery and Chemical Service," Materials Properties Council, FS-26, Draft No. 5, Consultants Report, NY, 1995.
3. G.M. Buchheim, "Ways to Deal with Wet H₂S Cracking Revealed by Study," *Oil and Gas Journal*, July 9, 1990, pp. 92–96.
4. R.B. Nielson et al., "Corrosion in Refinery Amine Systems," Paper No. 571, *Corrosion/95*, NACE International, Houston, TX.
5. NACE SP0472, *Methods and Controls to Prevent In-service Environmental Cracking of Carbon Steel Weldments in Corrosive Petroleum Refining Environments*, NACE International, Houston, TX.
6. NACE Publication 8X194, *Materials and Fabrication Practices for New Pressure Vessels used in Wet H₂S Refinery Service*, NACE International, Houston, TX.
7. R.D. Kane, R.J. Horvath, and M.S. Cayard, editors, *Wet H₂S Cracking of Carbon Steels and Weldments*, NACE International, Houston, TX, 1996.
8. NACE MR0103/ISO 17945, *Petroleum, petrochemical and natural gas industries—Metallic materials resistant to sulfide stress cracking in corrosive petroleum refining environments*, NACE International, Houston, TX.
9. D.J. Kotecki and D.G. Howden, *Submerged-arc-weld Hardness and Cracking in Wet Sulfide Service*, WRC Bulletin 184, Welding Research Council, Shaker Heights, OH, 1973.

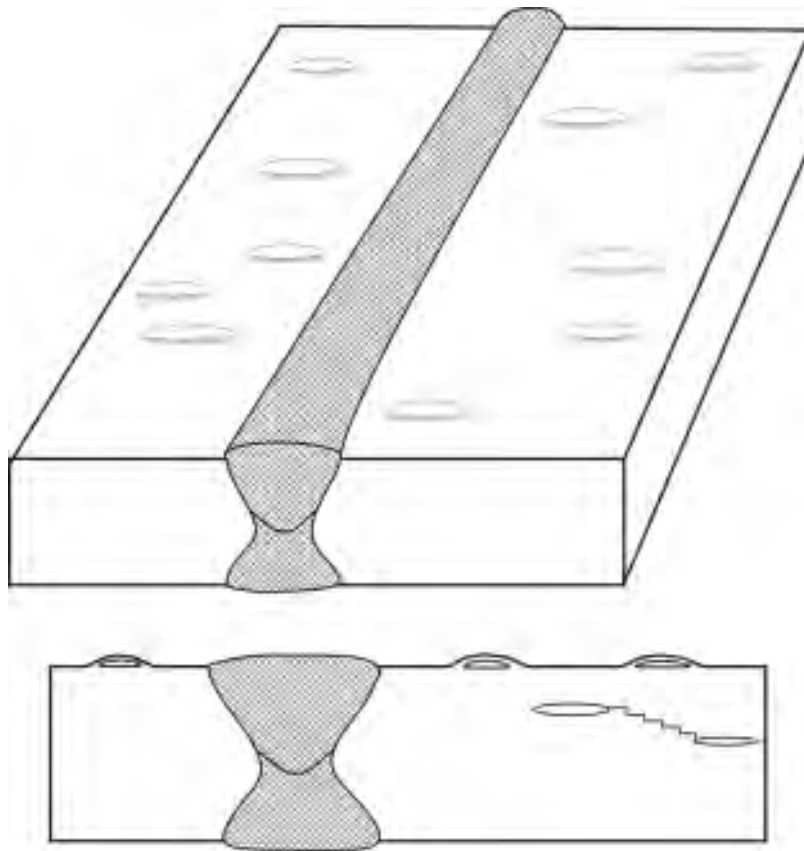


Figure 3-67-1—Illustration showing hydrogen blistering and HIC damage.

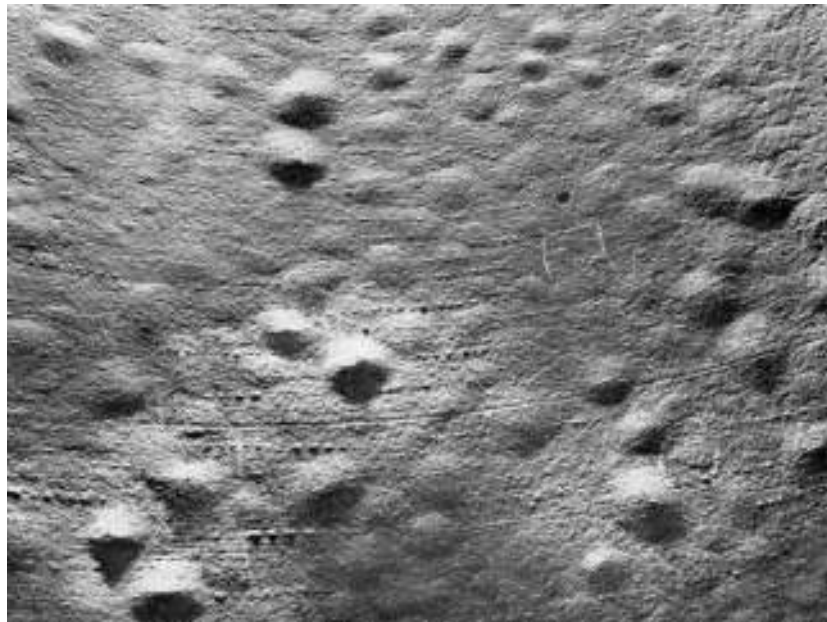


Figure 3-67-2—Extensive hydrogen blistering on the ID surface of a steel pressure vessel.



Figure 3-67-3—HIC damage as shown in the cross section of the shell of a trim cooler that had been cooling vapors off a hot high-pressure separator (HHPS) vessel in a hydroprocessing unit.

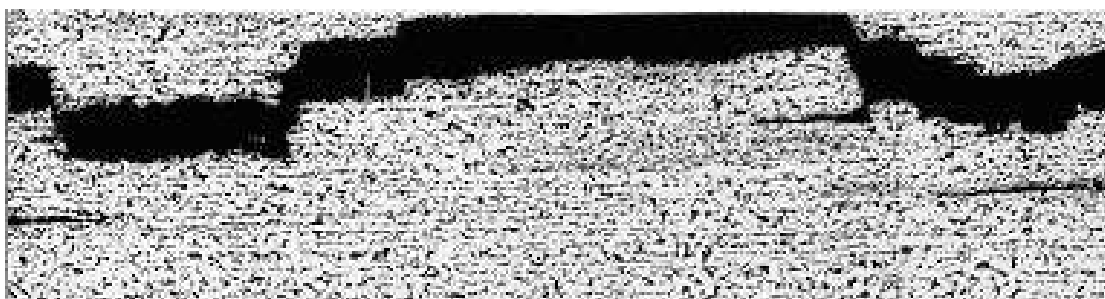


Figure 3-67-4—High-magnification photomicrograph of HIC damage.



Figure 3-67-5—High-magnification photomicrograph showing stepwise cracking nature of HIC damage.

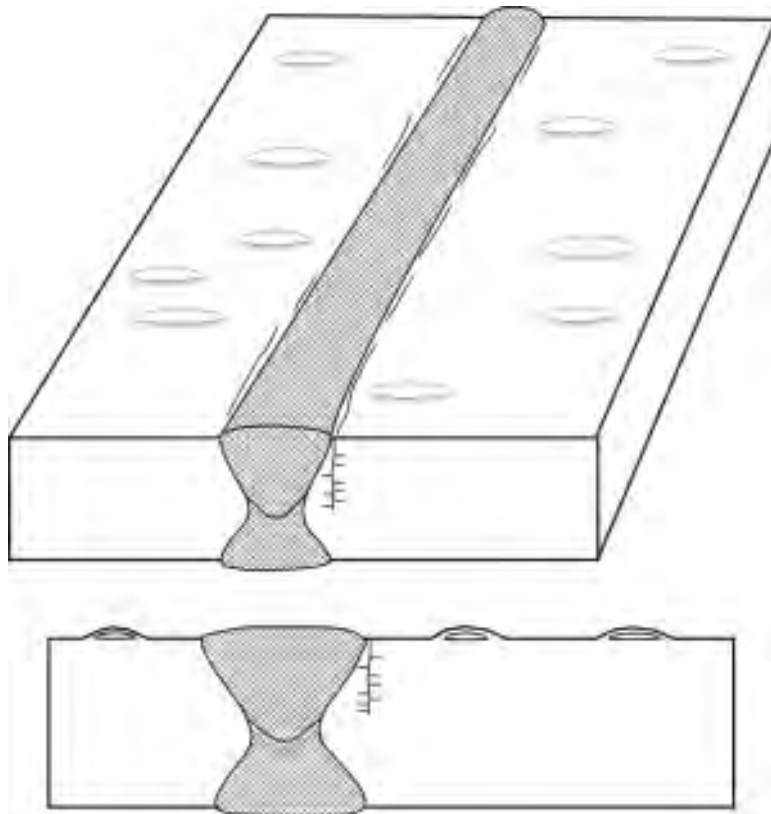


Figure 3-67-6—Illustration of hydrogen blistering that is accompanied by SOHIC damage at the weld.

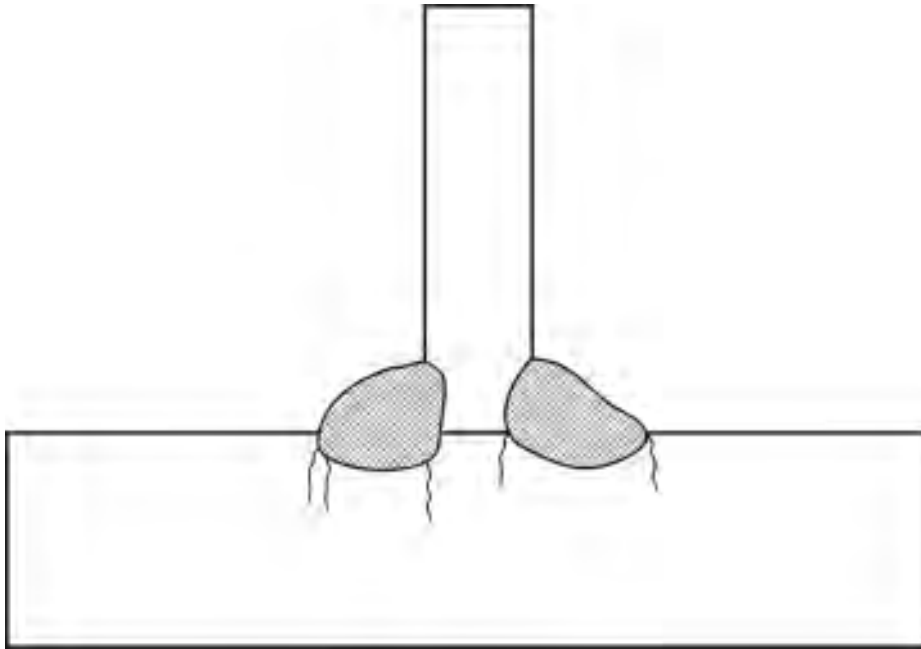


Figure 3-67-7—Illustration of SOHIC damage at a fillet weld that is usually a combination of SSC and SOHIC.



Figure3-67-8—Photograph showing WFMT indication of SOHIC damage.

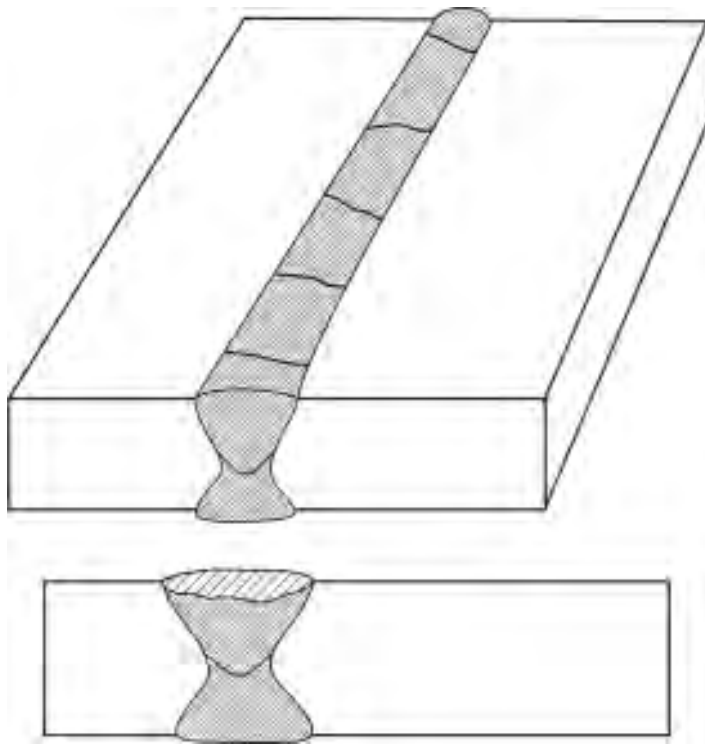


Figure 3-67-9—Illustration of SSC damage in a hard weld.

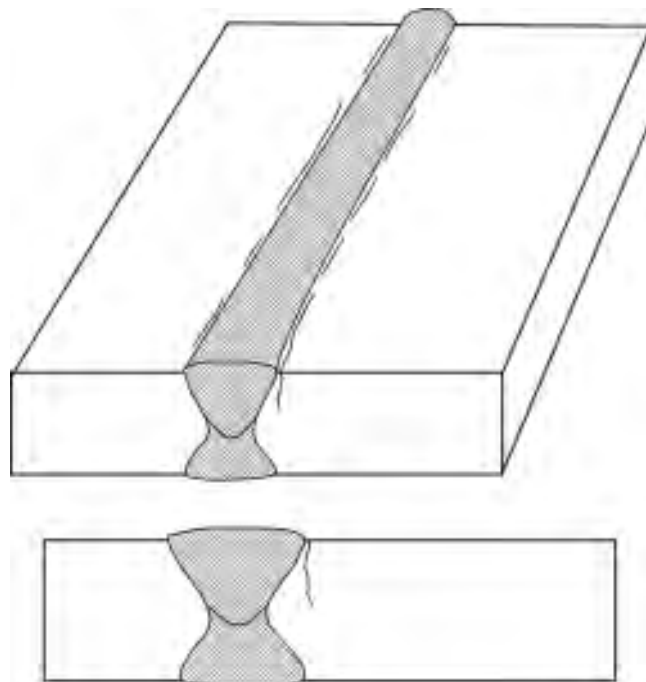


Figure 3-67-10—Illustration showing morphology of SSC in a hard HAZ.

4 Process Unit Process Flow Diagrams

Simplified process unit process flow diagrams (PFDs) for process units commonly found in many refineries are shown in this section. The PFDs are highlighted to show some of the areas within the unit where many of the primary damage mechanisms can be found. The reader should be advised that this is not intended to be an all-inclusive list of the damage mechanisms but should serve as a starting point for some of the major considerations.

The PFDs included in this section are listed below. A key to the Damage Mechanisms used on the PFDs is shown in [Table 4-1](#).

- Crude Unit/Vacuum: [Figure 4-1](#)
- Delayed Coker: [Figure 4-2](#)
- Fluid Catalytic Cracking: [Figure 4-3](#)
- FCC Light Ends Recovery: [Figure 4-4](#)
- Catalytic Reforming—Continuous Catalytic Reforming (CCR): [Figure 4-5](#)
- Catalytic Reforming—Fixed Bed: [Figure 4-6](#)
- Hydroprocessing Units—Hydrotreating, Hydrocracking: [Figure 4-7](#)
- Sulfuric Acid Alkylation: [Figure 4-8](#)
- HF Alkylation: [Figure 4-9](#)
- Amine Treating: [Figure 4-10](#)
- Sulfur Recovery: [Figure 4-11](#)
- Sour Water Stripper: [Figure 4-12](#)
- Isomerization: [Figure 4-13](#)
- Hydrogen Reforming: [Figure 4-14](#)
- Visbreaker: [Figure 4-15](#)
- Caustic Treating: [Figure 4-16](#)

Table 4-1—Key to Damage Mechanisms

DM#	Damage Mechanism	DM#	Damage Mechanism
1	Sulfidation	36	Sulfuric Acid Corrosion
2	Wet H ₂ S Damage (Blistering/HIC/SOHIC/SSC)	37	Hydrofluoric Acid Corrosion
3	Creep and Stress Rupture	38	Flue Gas Dew Point Corrosion
4	High-temperature H ₂ /H ₂ S Corrosion	39	Dissimilar Metal Weld Cracking
5	Polythionic Acid Stress Corrosion Cracking	40	Hydrogen Stress Cracking in Hydrofluoric Acid
6	Naphthenic Acid Corrosion	41	Dealloying (Dezincification; Denickelification)
7	Ammonium Bisulfide Corrosion (Alkaline Sour Water)	42	CO ₂ Corrosion
8	Ammonium Chloride Corrosion	43	Corrosion Fatigue
9	Hydrochloric Acid Corrosion	44	Fuel Ash Corrosion
10	High-temperature Hydrogen Attack	45	Amine Corrosion
11	Oxidation	46	Corrosion Under Insulation
12	Thermal Fatigue	47	Atmospheric Corrosion
13	Sour Water Corrosion (Acidic)	48	Ammonia Stress Corrosion Cracking
14	Refractory Degradation	49	Cooling Water Corrosion
15	Graphitization	50	Boiler Water and Condensate Corrosion
16	Temper Embrittlement	51	Microbiologically Influenced Corrosion
17	Decarburization	52	Liquid Metal Embrittlement
18	Caustic Stress Corrosion Cracking	53	Galvanic Corrosion
19	Caustic Corrosion	54	Mechanical Fatigue (Includes Vibration Fatigue)
20	Erosion/Erosion-Corrosion	55	Nitriding
21	Carbonate Stress Corrosion Cracking (ACSCC)	56	Vibration-Induced Fatigue Withdrawn. See #54
22	Amine Stress Corrosion Cracking	57	Titanium Hydriding
23	Chloride Stress Corrosion Cracking	58	Soil Corrosion
24	Carburization	59	Metal Dusting
25	Hydrogen Embrittlement	60	Strain Aging
26	Steam Blanketing Withdrawn. See #30.	61	Sulfate Stress Corrosion Cracking Withdrawn
27	Thermal Shock	62	Phosphoric Acid Corrosion
28	Cavitation	63	Phenol (Carbolic Acid) Corrosion
29	Graphitic Corrosion of Cast Irons	64	Ethanol Stress Corrosion Cracking
30	Short-term Overheating—Stress Rupture (Including Steam Blanketing)	65	Gaseous Oxygen-enhanced Ignition and Combustion
31	Brittle Fracture	66	Aqueous Organic Acid Corrosion
32	Sigma Phase Embrittlement	67	Brine Corrosion
33	885 °F (475 °C) Embrittlement	68	Concentration Cell Corrosion
34	Spheroidization (Softening)	69	Hydrofluoric Acid Stress Corrosion Cracking of Nickel Alloys
35	Stress Relaxation Cracking (Reheat Cracking)	70	Oxygenated Water Corrosion (Non-boiler)

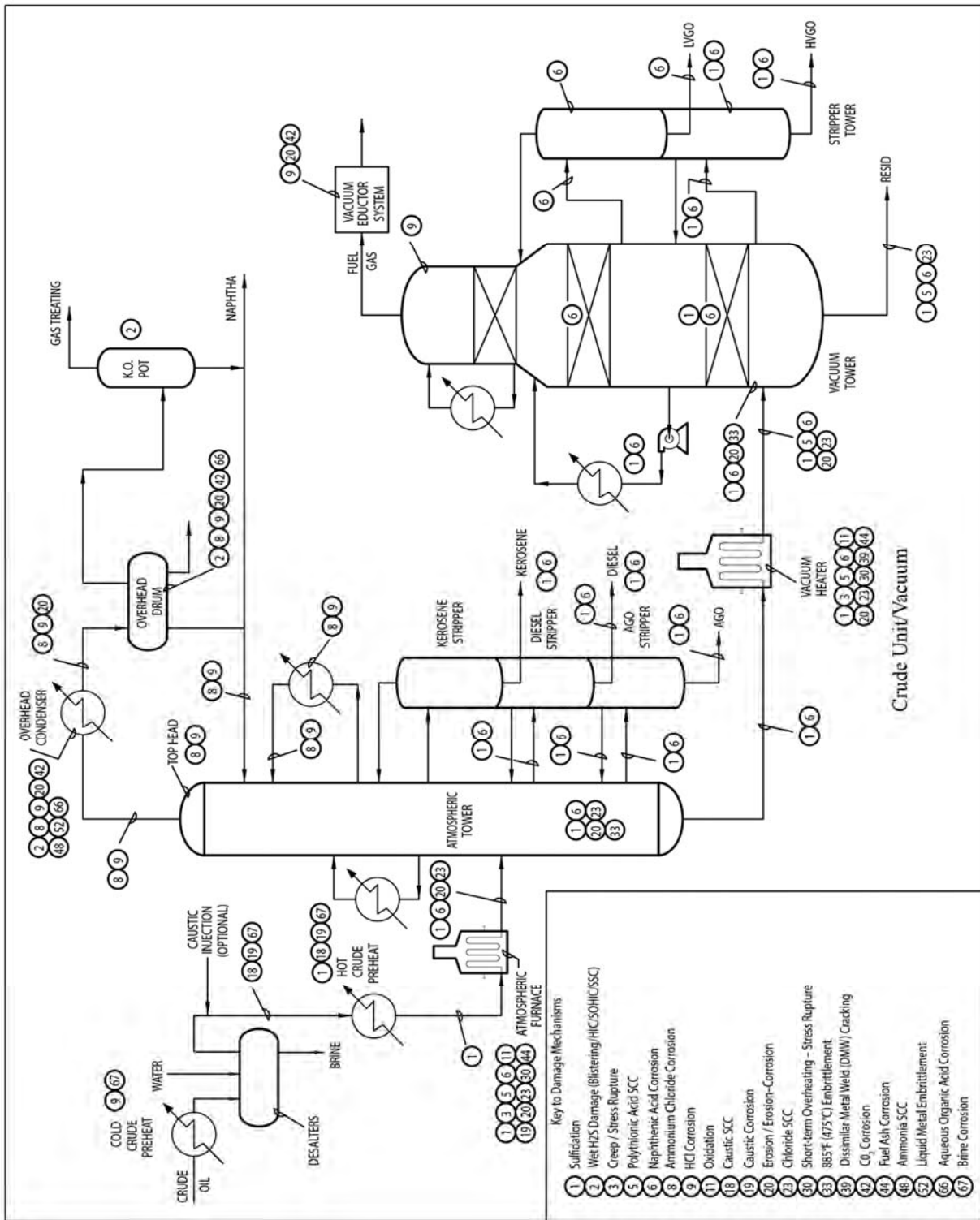


Figure 4-1—Crude Unit/Vacuum

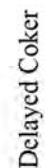


Figure 4-2—Delayed Coker



Figure 4-3—Fluid Catalytic Cracking

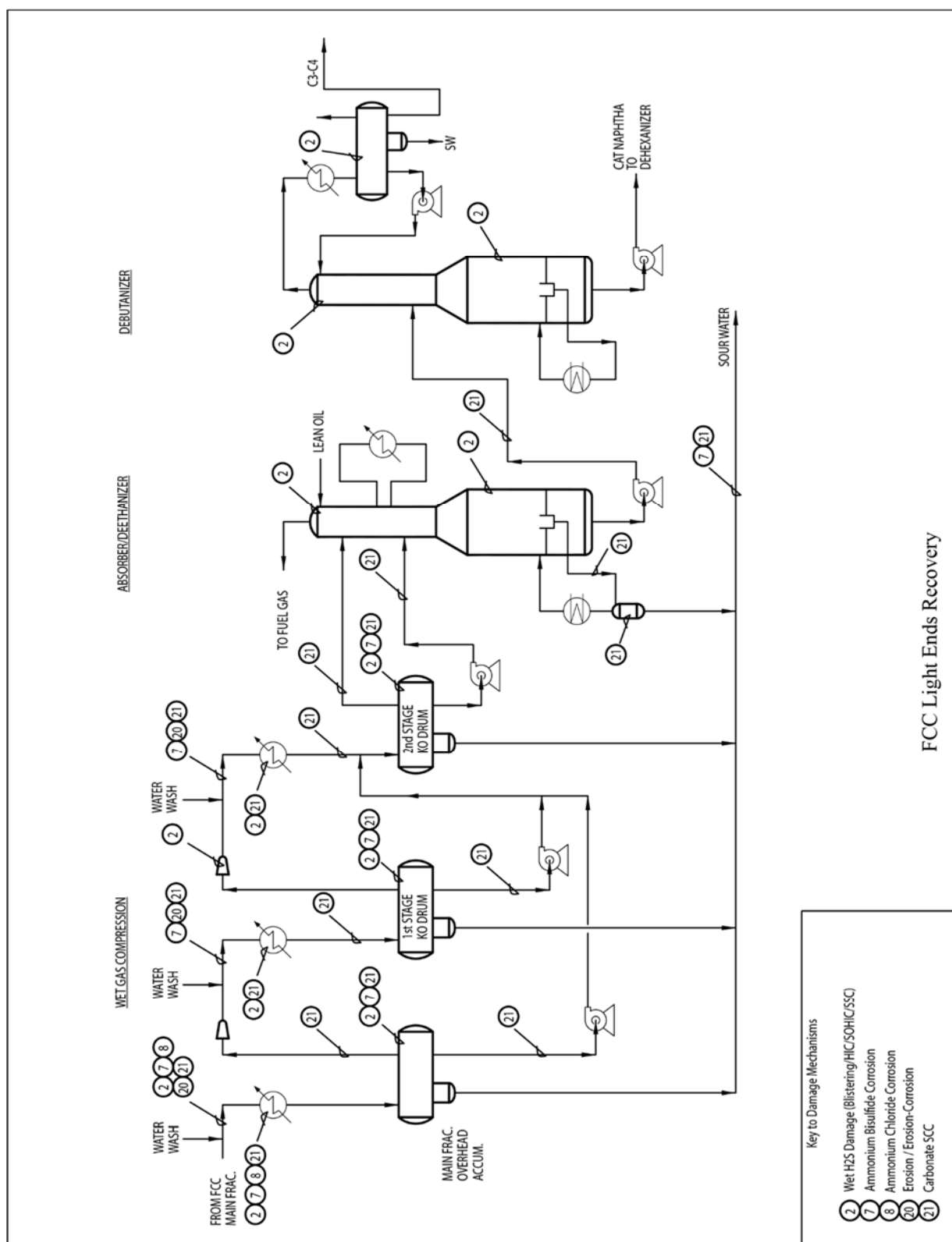


Figure 4-4—FCC Light Ends Recovery

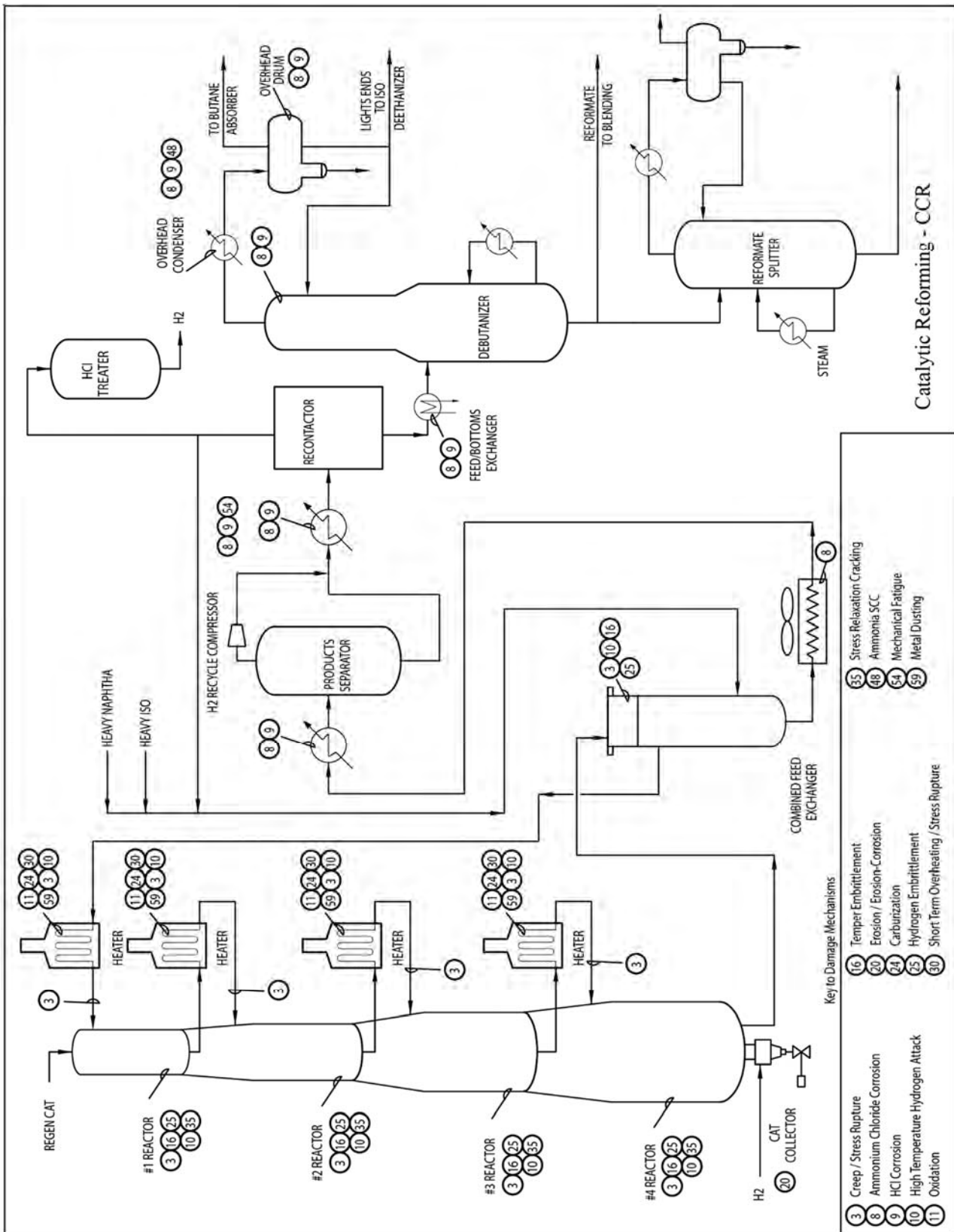


Figure 4-5—Catalytic Reforming—Continuous Catalytic Reforming (CCR)

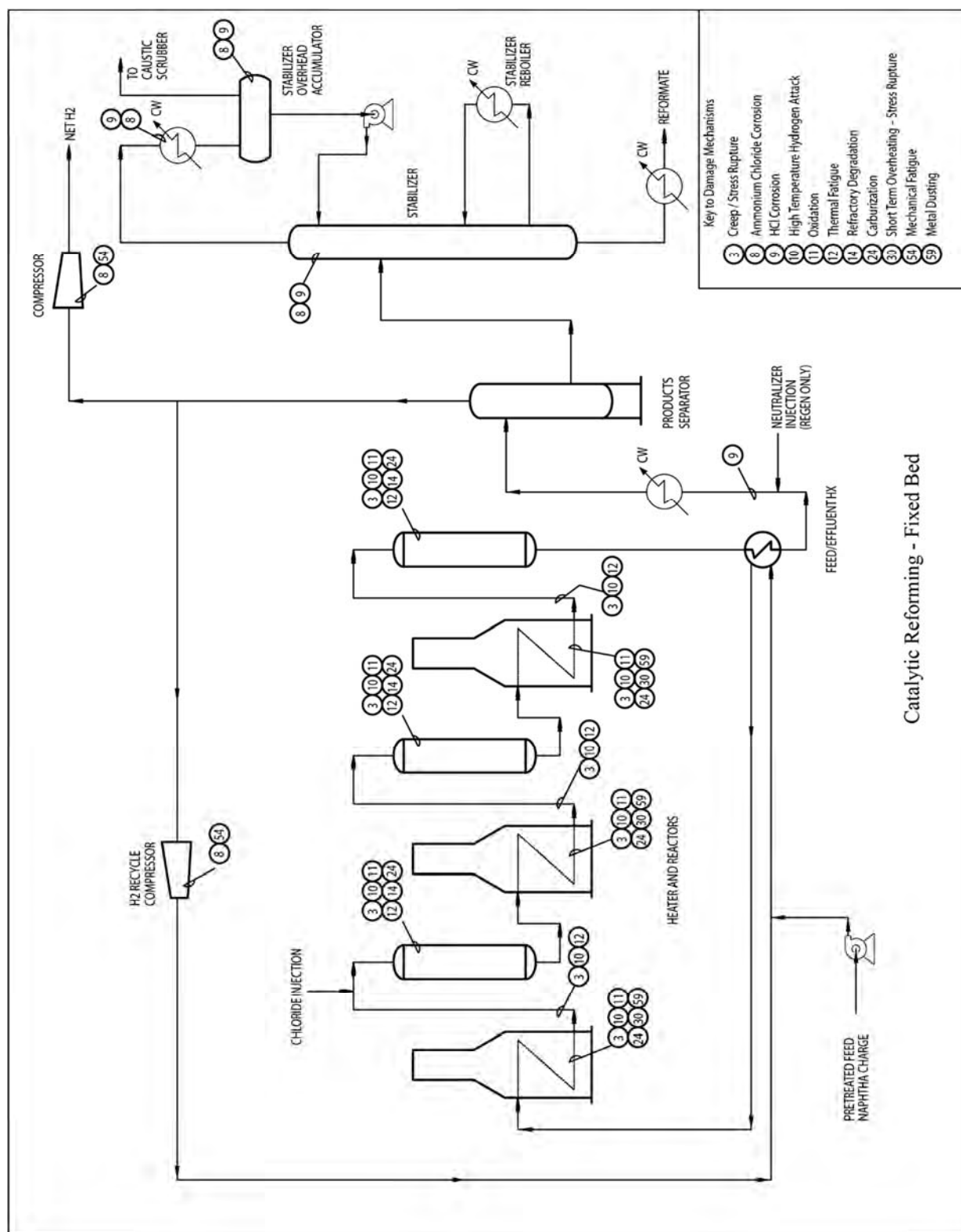


Figure 4-6—Catalytic Reforming—Fixed Bed

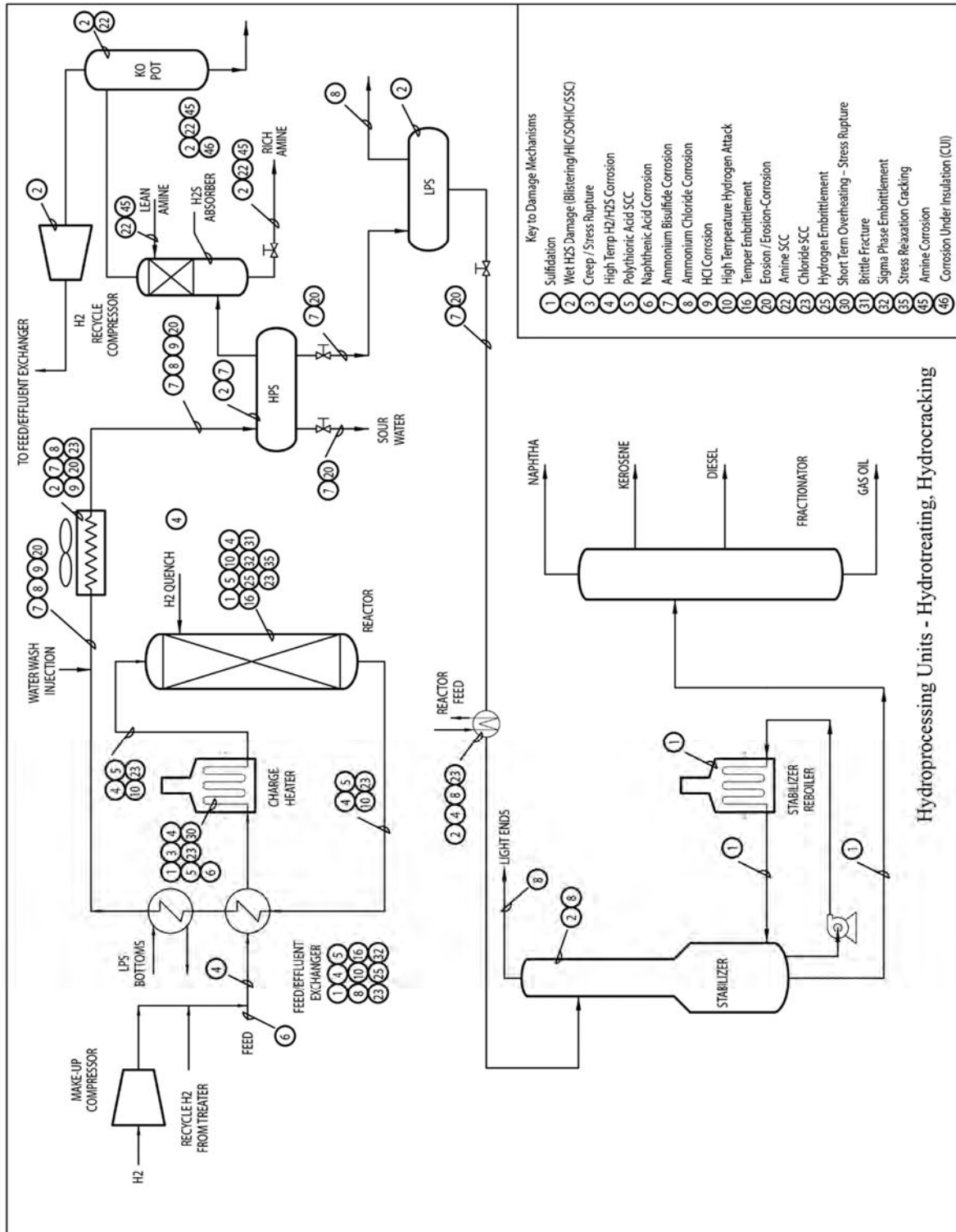


Figure 4-7—Hydroprocessing—Hydrotreating, Hydrocracking

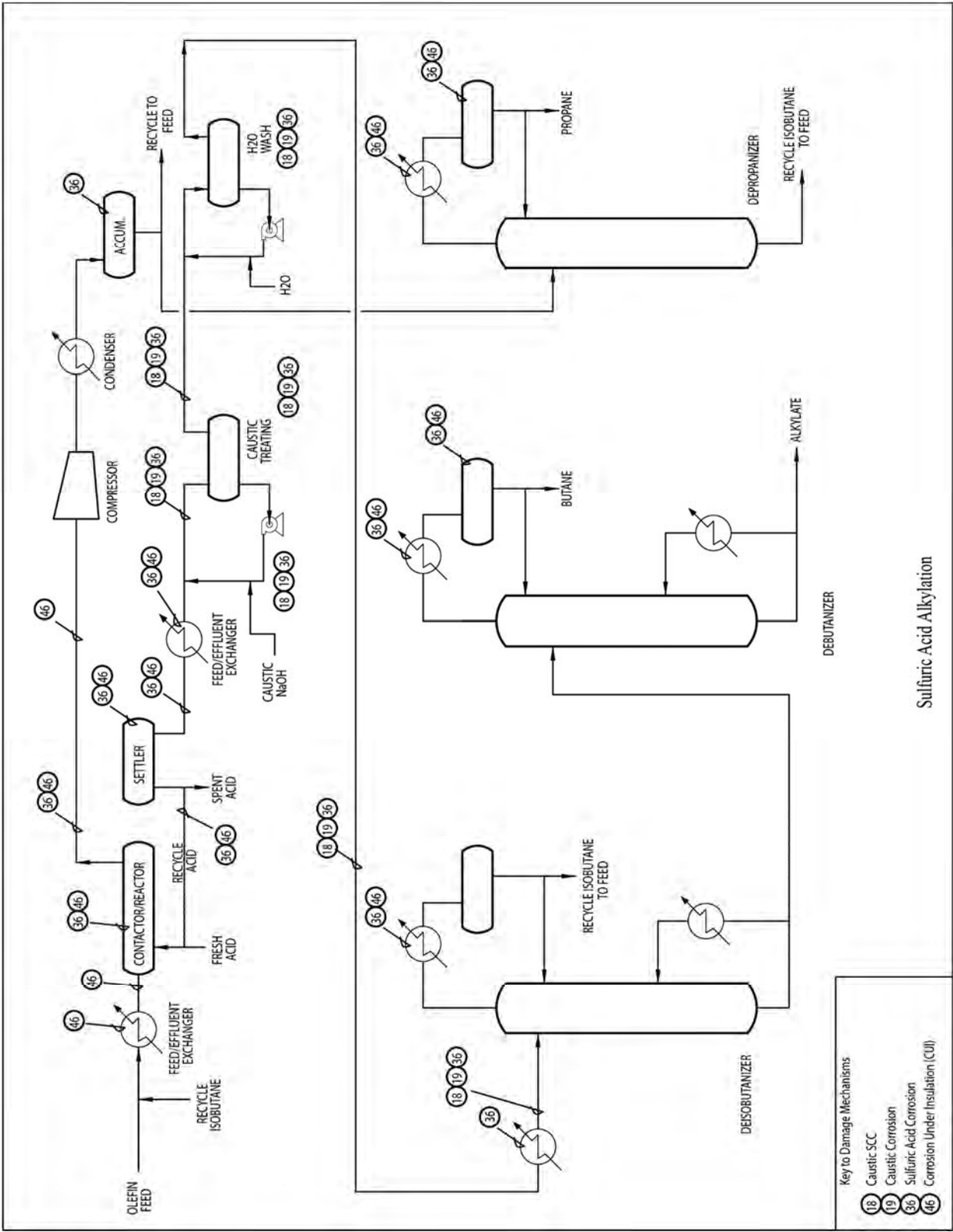


Figure 4-8—Sulfuric Acid Alkylation

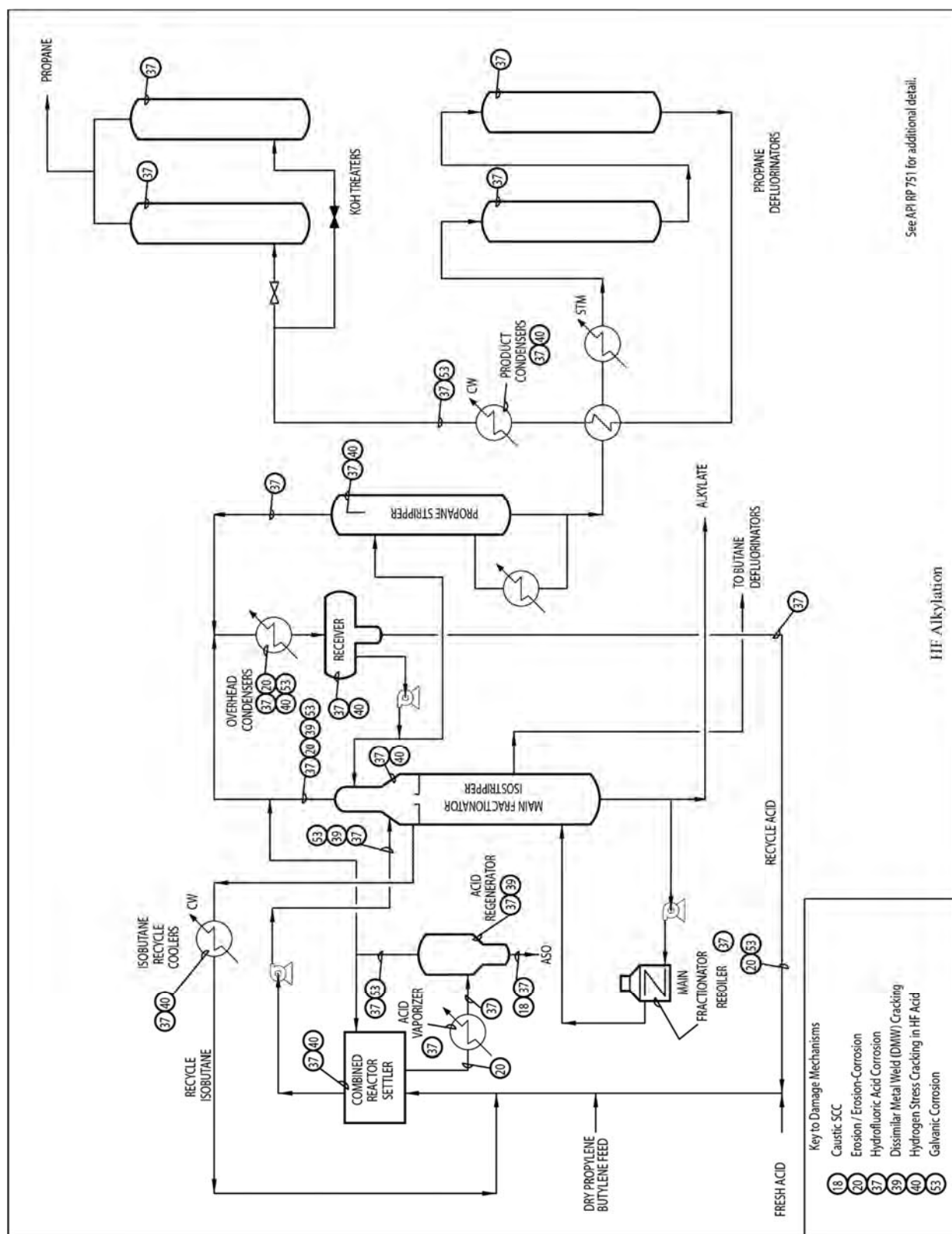


Figure 4-9—HF Alkylation

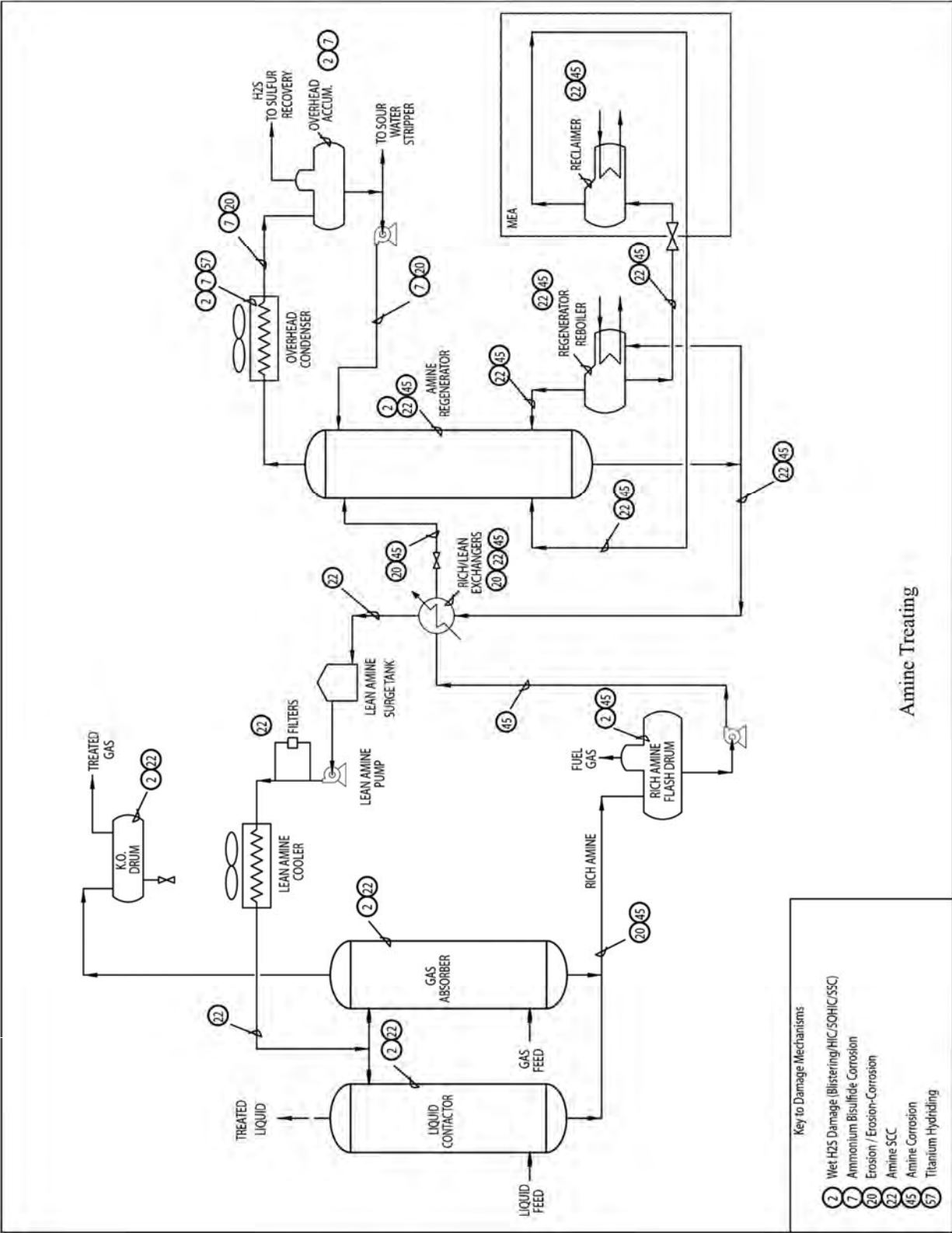


Figure 4-10—Amine Treating

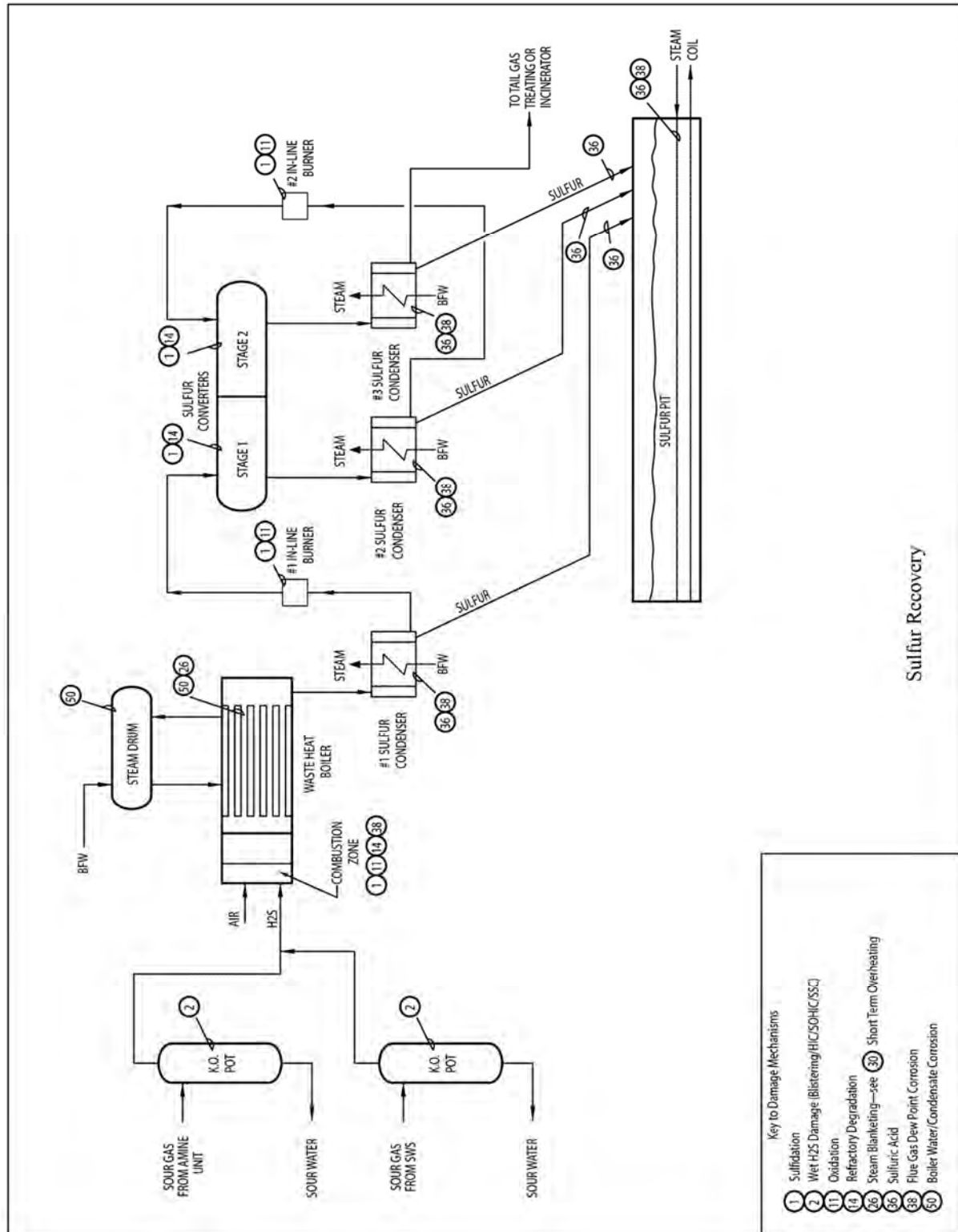


Figure 4-11—Sulfur Recovery

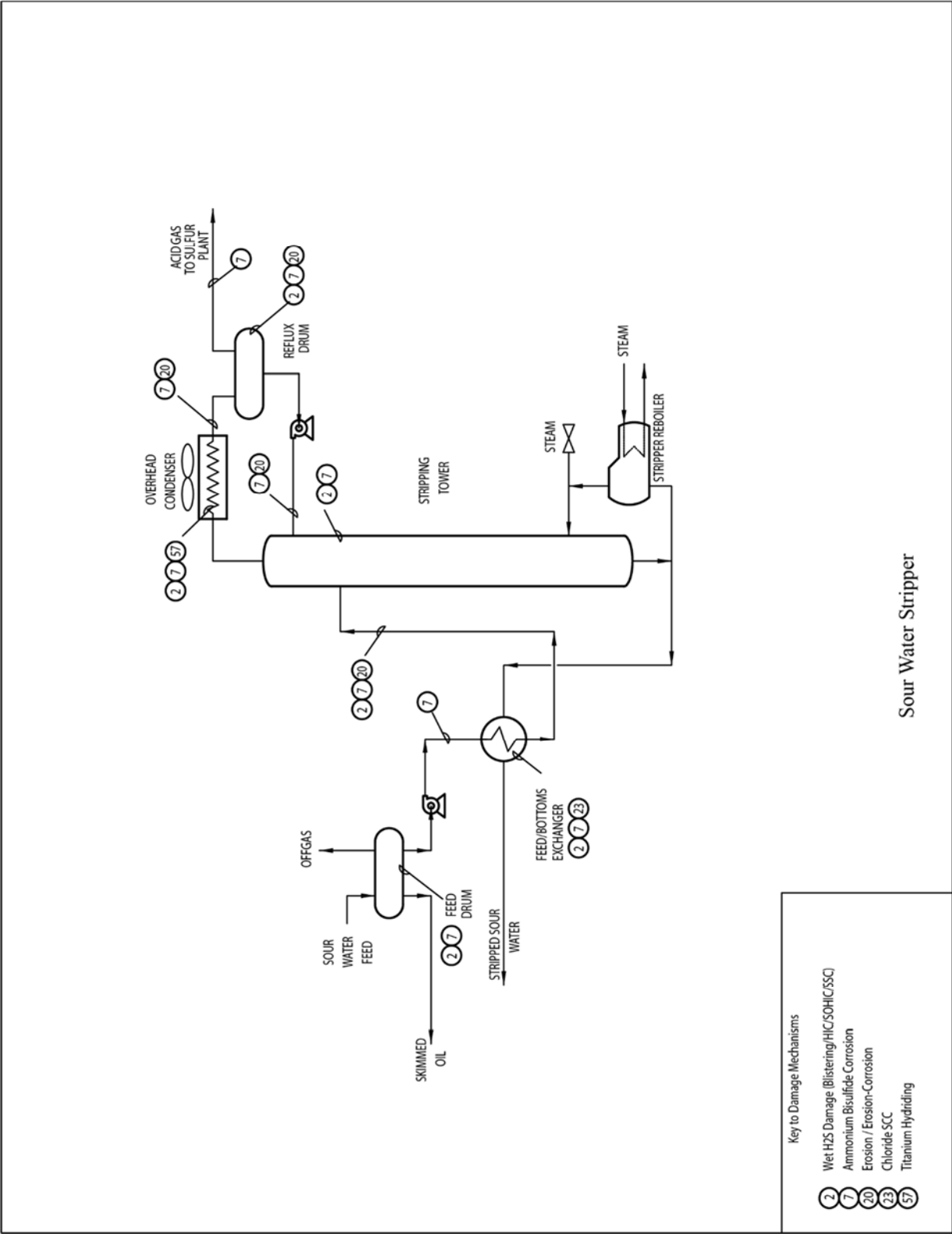


Figure 4-12—Sour Water Stripper

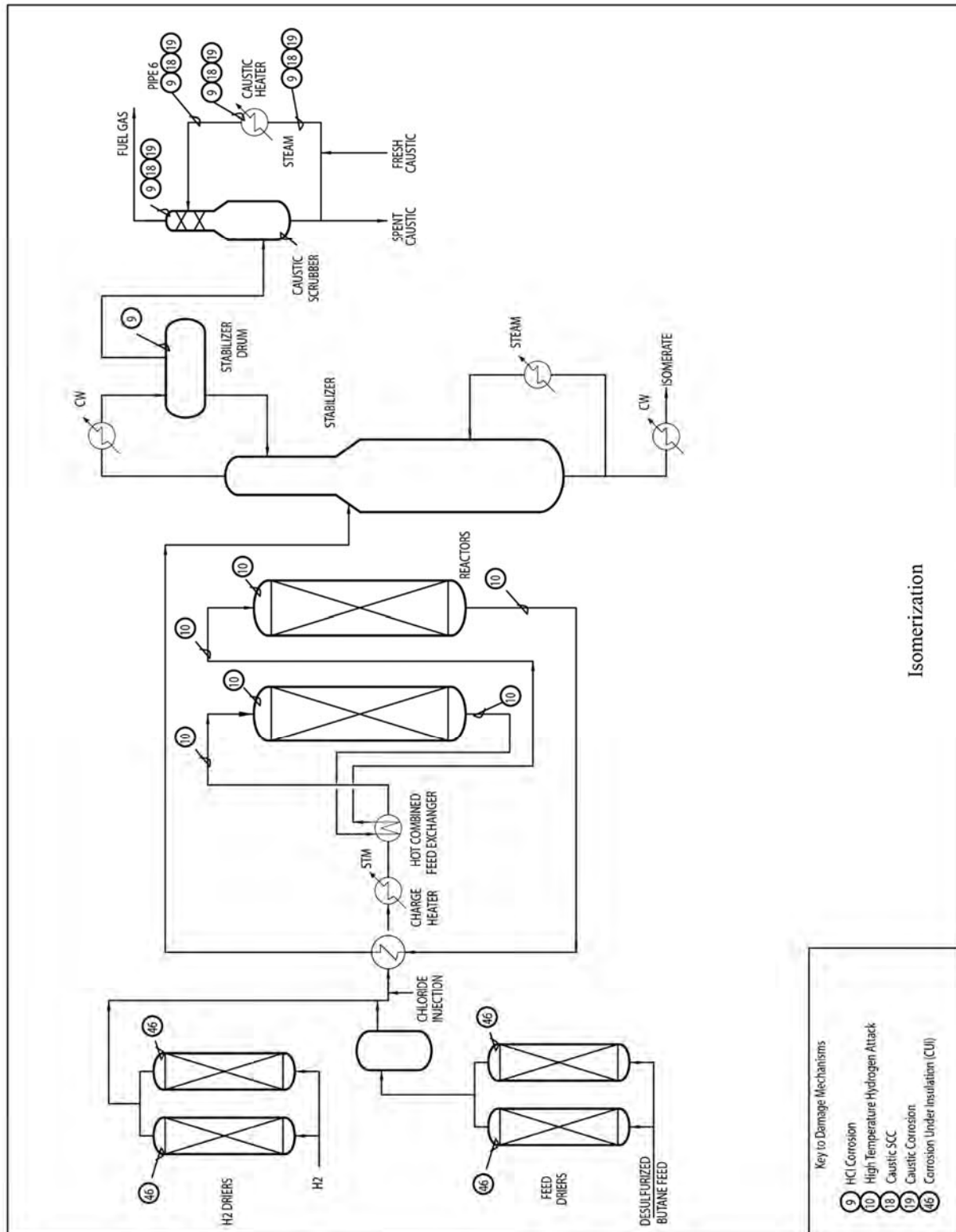


Figure 4-13—Isomerization

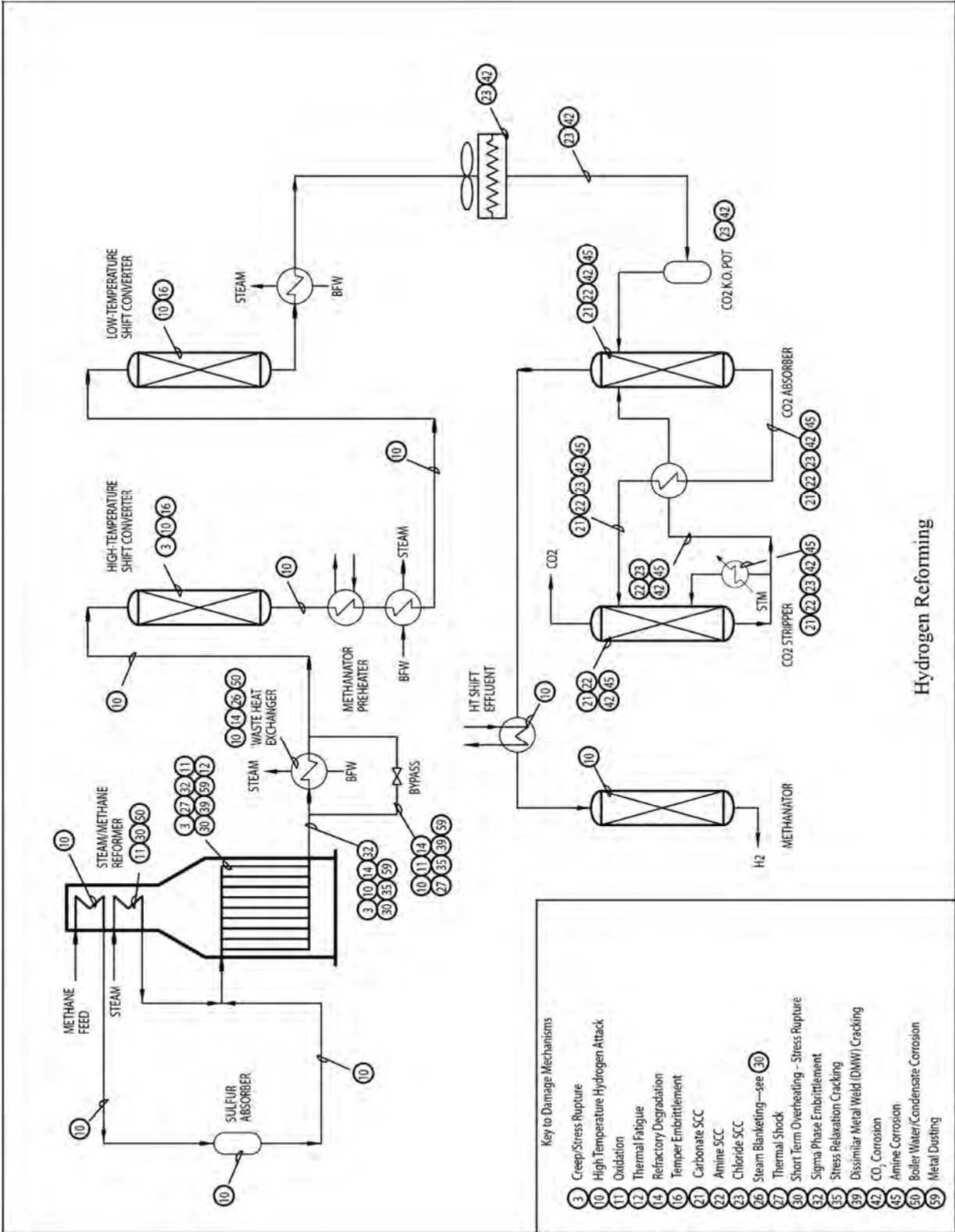


Figure 4-14—Hydrogen Reforming

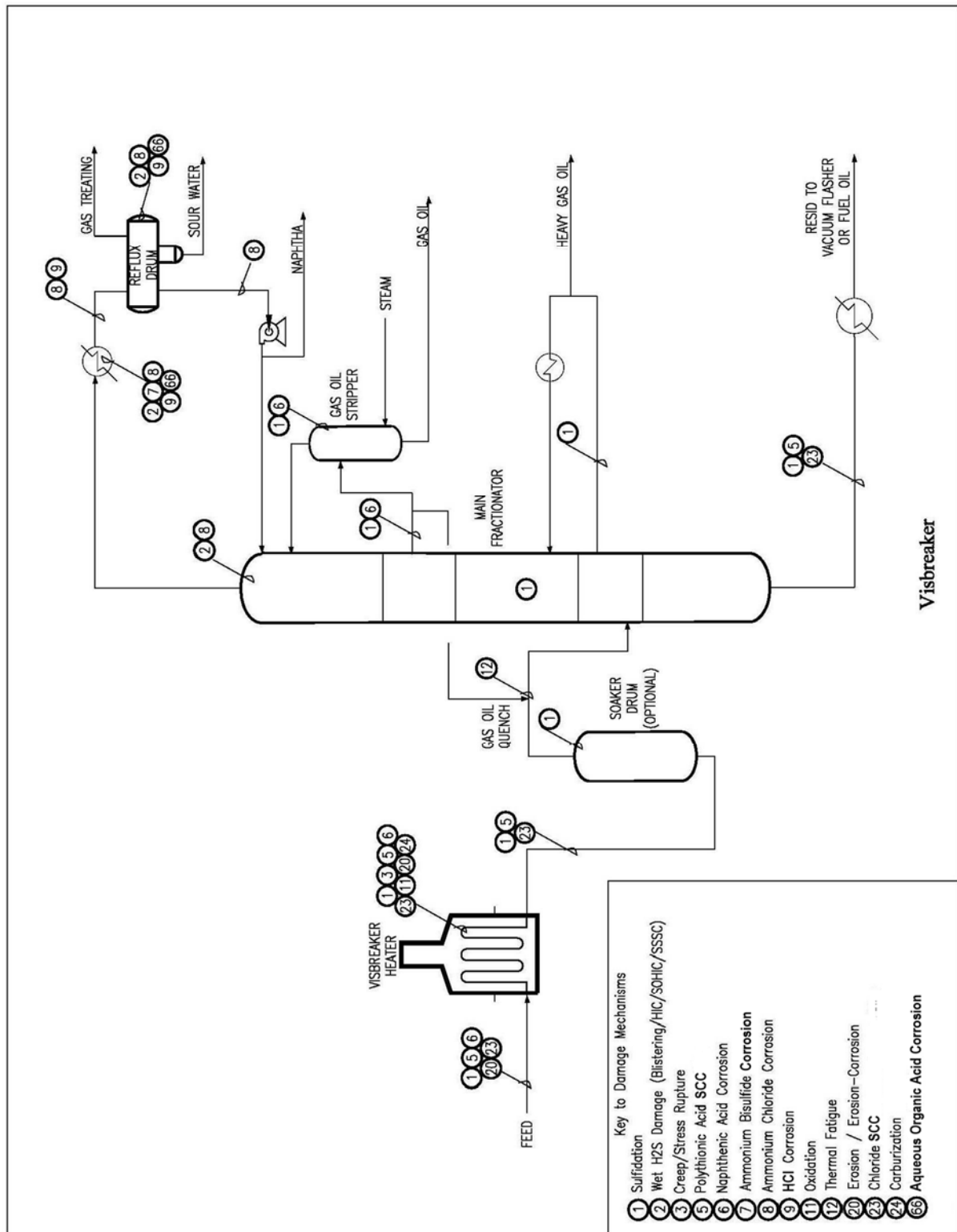


Figure 4-15—Visbreaker

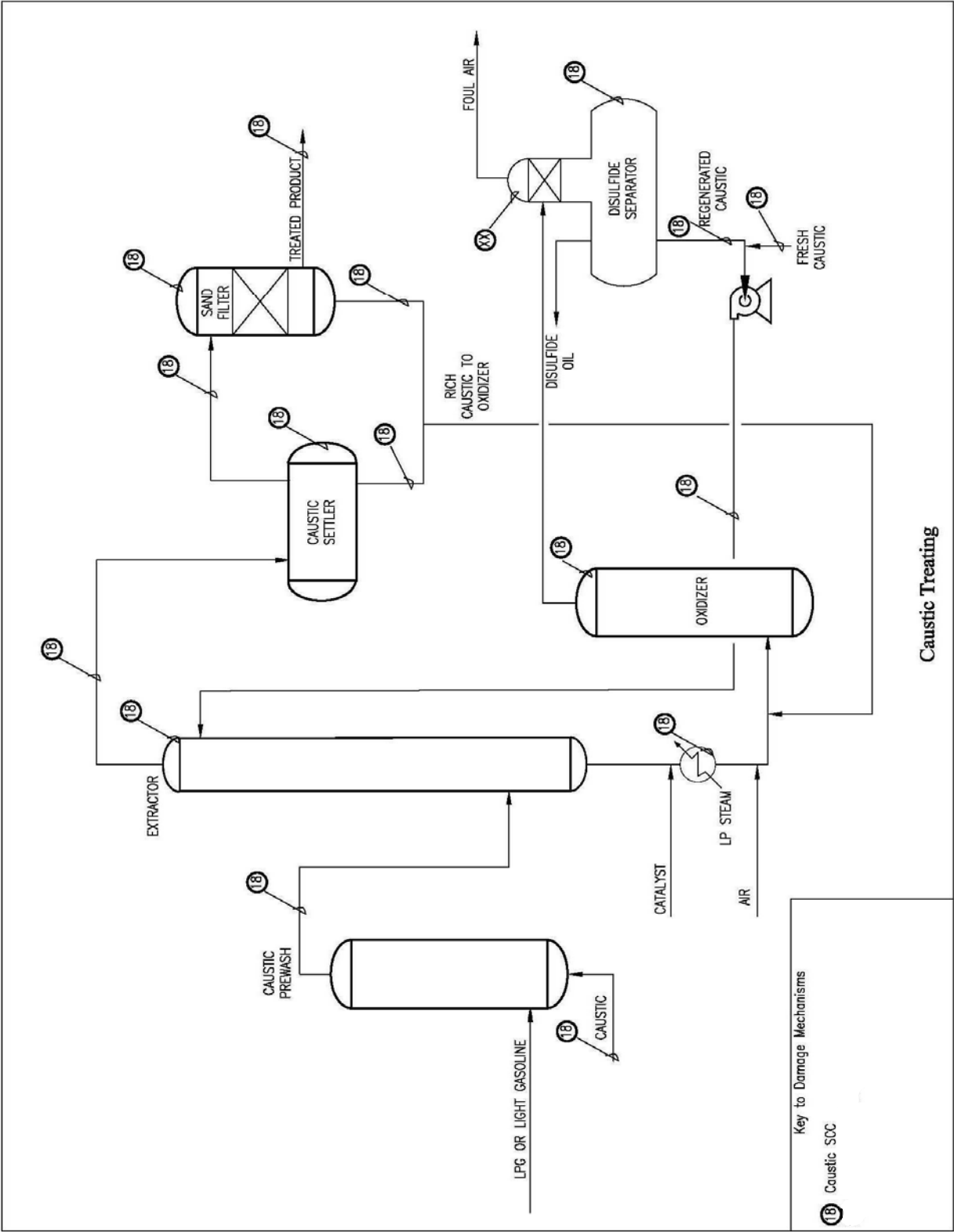


Figure 4-16—Caustic Treating

Annex A

(informative)

Useful Standards and References Relevant to this Recommended Practice

A.1 Codes and Standards

A.1.1 General

The following standards, codes, specifications, and other documents, some of which are cited in this recommended practice, provide useful information related to the subject matter of this recommended practice.

A.1.2 American Petroleum Institute Publications

API 510, *Pressure Vessel Inspection Code: In-service Inspection, Rating, Repair, and Alteration*

API Standard 530, *Calculation of Heater-tube Thickness in Petroleum Refineries*

API 570, *Piping Inspection Code: In-service Inspection, Repair, and Alteration of Piping Systems*

API Recommended Practice 572, *Inspection Practices for Pressure Vessels*

API Recommended Practice 573, *Inspection of Fired Boilers and Heaters*

API Recommended Practice 574, *Inspection Practices for Piping System Components*

API Recommended Practice 575, *Inspection Practices for Atmospheric and Low-pressure Storage Tanks*

API Recommended Practice 576, *Inspection of Pressure-relieving Devices*

API Recommended Practice 577, *Welding Inspection and Metallurgy*

API Recommended Practice 578, *Guidelines for a Material Verification Program (MVP) for New and Existing Assets*

API Recommended Practice 580, *Risk-Based Inspection*

API Recommended Practice 581, *Risk-Based Inspection Methodology*

API Recommended Practice 582, *Welding Guidelines for the Chemical, Oil, and Gas Industries*

API Recommended Practice 583, *Corrosion Under Insulation and Fireproofing*

API Recommended Practice 584, *Integrity Operating Windows*

API Recommended Practice 585, *Pressure Equipment Integrity Incident Investigation*

API 579-1/ASME FFS-1, *Fitness-For-Service*

API Standard 653, *Tank Inspection, Repair, Alteration, and Reconstruction*

API Standard 660, *Shell-and-Tube Heat Exchangers*

API Recommended Practice 751, *Safe Operation of Hydrofluoric Acid Alkylation Units*

API Technical Report 932-A, *A Study of Corrosion in Hydroprocess Reactor Effluent Air Cooler Systems*

API Recommended Practice 932-B, *Design, Materials, Fabrication, Operation, and Inspection Guidelines for Corrosion Control in Hydroprocessing Reactor Effluent Air Cooler (REAC) Systems*

API Recommended Practice 934-A, *Materials and Fabrication of 2¼Cr-1Mo, 2¼Cr-1Mo-¼V, 3Cr-1Mo, and 3Cr-1Mo-¼V Steel Heavy Wall Pressure Vessels for High-temperature, High-pressure Hydrogen Service*

API Technical Report 934-B, *Fabrication Considerations for Vanadium-Modified Cr-Mo Steel Heavy Wall Pressure Vessels*

API Recommended Practice 934-C, *Materials and Fabrication of 1¼Cr-½Mo Steel Heavy Wall Pressure Vessels for High-pressure Hydrogen Service Operating at or Below 825 °F (441 °C)*

API Technical Report 934-D, *Technical Report on the Materials and Fabrication Issues of 1¼Cr-½Mo and 1Cr-½Mo Steel Pressure Vessels*

API Recommended Practice 934-E, *Recommended Practice for Materials and Fabrication of 1¼Cr-½Mo Steel Pressure Vessels for Service Above 825 °F (440 °C)*

API Technical Report 934-G, *Design, Fabrication, Operational Effects, Inspection, Assessment, and Repair of Coke Drums and Peripheral Components in Delayed Coking Units*

API Publication 938-A, *Experimental Study of Causes and Repair of Cracking of 1¼Cr-½Mo Steel Equipment*

API Publication 938-B, *Use of 9Cr-1Mo-V (Grade 91) Steel in the Oil Refining Industry*

API Technical Report 938-C, *Use of Duplex Stainless Steels in the Oil Refining Industry*

API Technical Report 939-A, *Research Report on Characterization and Monitoring of Cracking in Wet H₂S Service*

API Technical Report 939-B, *Repair and Remediation Strategies for Equipment Operating in Wet H₂S Service*

API Recommended Practice 939-C, *Guidelines for Avoiding Sulfidation (Sulfidic) Corrosion Failures in Oil Refineries*

API Technical Report 939-D, *Stress Corrosion Cracking of Carbon Steel in Fuel-grade Ethanol: Review, Experience Survey, Field Monitoring, and Laboratory Testing*

API Bulletin 939-E, *Identification, Repair, and Mitigation of Cracking of Steel Equipment in Fuel Ethanol Service*

API Recommended Practice 941, *Steels for Hydrogen Service at Elevated Temperatures and Pressures in Petroleum Refineries and Petrochemical Plants*

API Technical Report 941, *The Technical Basis Document for API RP 941*

API Technical Report 942-A, *Materials, Fabrication, and Repair Considerations for Hydrogen Reformer Furnace Outlet Pigtails and Manifolds*

API Technical Report 942-B, *Material, Fabrication, and Repair Considerations for Austenitic Alloys Subject to Embrittlement and Cracking in High Temperature 565 °C to 760 °C (1050 °F to 1400 °F) Refinery Services*

API Recommended Practice 945, *Avoiding Environmental Cracking in Amine Units*

A.1.3 Other Publications

*ASM Handbook*¹, Volume 1—*Properties and Selection: Iron, Steels, and High-performance Alloys*; Volume 11—*Failure Analysis and Prevention*; Volume 13—*Corrosion*

*ASME Boiler and Pressure Vessel Code (BPVC)*², Section VIII: *Rules for Construction of Pressure Vessels; Divisions 1 & 2*

*ASTM MNL41*³, *Fracture and Fatigue Control in Structures: Applications of Fracture Mechanics*

ASTM STP1428, Thermomechanical Fatigue Behavior of Materials

*BS 7910*⁴, *Guide to Methods for Assessing the Acceptability of Flaws in Metallic Structures*

*MPC Report FS-26*⁵, *Fitness-For Service Evaluation Procedures for Operating Pressure Vessels, Tanks, and Piping in Refinery and Chemical Service*

*NACE MR0103*⁶/*ISO 17945*⁷, *Petroleum, petrochemical and natural gas industries—Metallic materials resistant to sulfide stress cracking in corrosive petroleum refining environments*

NACE Publication 5A151, Materials of Construction for Handling Sulfuric Acid

NACE Publication 5A171, Materials for Storing and Handling Commercial Grades of Aqueous Hydrofluoric Acid and Anhydrous Hydrogen Fluoride

NACE Publication 8X194, Materials and Fabrication Practices for New Pressure Vessels Used in Wet H₂S Refinery Service

NACE Publication 34105, Effect of Nonextractable Chlorides on Refinery Corrosion and Fouling

NACE Publication 34108, Review and Survey of Alkaline Carbonate Stress Corrosion Cracking in Refinery Sour Waters

NACE SP0169, Control of External Corrosion on Underground or Submerged Metallic Piping Systems

NACE SP0170, Protection of Austenitic Stainless Steels and Other Austenitic Alloys from Polythionic Acid Stress Corrosion Cracking During a Shutdown of Refinery Equipment

NACE SP0198, Control of Corrosion Under Thermal Insulation and Fireproofing Materials—A Systems Approach

NACE SP0294, Design, Fabrication, and Inspection of Storage Tank Systems for Concentrated Fresh and Process Sulfuric Acid and Oleum at Ambient Temperatures

NACE SP0296, Detection, Repair, and Mitigation of Cracking in Refinery Equipment in Wet H₂S Environments

NACE SP0403, Avoiding Caustic Stress Corrosion Cracking of Refinery Equipment and Piping

¹ ASM International, 9639 Kinsman Road, Materials Park, OH 44073-0002, www.asminternational.org.

² ASME International, 2 Park Avenue, New York, NY 10016-5990, www.asme.org.

³ ASTM International, 100 Barr Harbor Drive, West Conshohocken, PA 19428-2959, www.astm.org.

⁴ British Standard Institution, 389 Chiswick High Road, London W4 4AL, UK, www.bsi-global.com.

⁵ Materials Properties Council (part of the Welding Research Council), P.O. Box 201547, Shaker Heights, OH 44122, www.forengineers.org/mpc.

⁶ NACE International, 15835 Park Ten Place, Houston, TX 77084, www.nace.org.

⁷ International Organization for Standardization, 1, ch. de la Voie-Creuse, Case postale 56, CH-1211 Geneva 20, Switzerland, www.iso.org.

NACE SP0472, *Methods and Controls to Prevent In-service Environmental Cracking of Carbon Steel Weldments in Corrosive Petroleum Refining Environments*

NACE SP0590, *Prevention, Detection, and Correction of Deaerator Cracking*

WRC Bulletin 032 ⁸, *Part 1: Graphitization of Steel in Petroleum Refining Equipment*

WRC Bulletin 275, *The Use of Quenched and Tempered 2¼Cr-1Mo Steel for Thick Wall Reactor Vessels in Petroleum Refinery Processes: An Interpretive Review of 25 Years of Research and Application*

WRC Bulletin 350, *Design Criteria for Dissimilar Metal Welds*

WRC Bulletin 409, *Fundamental Studies of the Metallurgical Causes and Mitigation of Reheat Cracking in 1¼Cr-½Mo and 2¼Cr-1Mo Steels*

WRC Bulletin 418, *Part 1: Constraint Effects on Fracture Behavior: The Effect of Crack Depth (a) and Crack-depth to Width Ratio (a/W) on the Fracture Toughness of A533-B Steel*

WRC Bulletin 452, *Recommended Practices for Local Heating of Welds in Pressure Vessels*

⁸ Welding Research Council, P.O. Box 201547, Shaker Heights, OH 44122, www.forengineers.org/wrc.

Annex B **(informative)**

Technical Inquiries

B.1 Introduction

API will consider written requests for interpretations of API 571. The API staff will make such interpretations in writing after consulting, if necessary, with the appropriate committee officers and committee members. The API committee responsible for maintaining API 571 meets regularly to consider written requests for interpretations and revisions and to develop new criteria dictated by technological development. The committee's activities in this regard are limited strictly to interpretations of the document and to the consideration of revisions to the current edition of the document on the basis of new data or technology. As a matter of policy, API does not approve, certify, rate, or endorse any item, construction, proprietary device, or activity, and, accordingly, inquiries that require such consideration will be returned. Moreover, API does not act as a consultant on specific engineering problems or on the general understanding or application of API 571. If, based on the inquiry information submitted, it is the opinion of the committee that the inquirer should seek other assistance, the inquiry will be returned with the recommendation that such assistance be obtained. All inquiries that cannot be understood because they lack information will be returned.

B.2 Inquiry Format

B.2.1 Inquiries shall be limited strictly to requests for interpretation of API 571 or to the consideration of revisions to the document on the basis of new data or technology. Inquiries shall be submitted in the format described in B.2.2.

B.2.2 The process for submitting a technical inquiry is explained in detail on the API website at: <http://rfi.api.org/>. Please read the information on this page for any updates to the process. You may also access an online form for submitting your request.



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